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MODELLING THE CURE OF NARMCO 5208:

A METHOD FOR DETERMINING THE CHEMICAL STATE OF THE PREPREG

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SUMMARY

The accurate modelling of the curing process of a thermoset resin system requires that the initial chemical state of the resin be properly characterized. In this work, a method has been developed for the epoxy/amine system Narmco 5208 which enables the use of data obtained by reverse-phase liquid chromatography (RPLC) to calculate the parameters required to describe the state of the resin. This was done by mathematically analyzing the chemical kinetics of the system in order to develop a simplified model relating the RPLC data to the unknown parameters, and then by preparing and analyzing a set of mixtures in order to verify the model and determine the specific numeric factors needed. The two most important parameters involved are the epoxy-to-hardener ratio and the initial degree of polymerization of the resin, both of which can vary from batch to batch. These are determined with a good degree of accuracy. Because of certain complications associated with the minor epoxy resin, the individual contents of the two epoxy resins present are determined with somewhat less precision. While the exact details of the method are specific to Narmco 5208, the general principles can be applied to other systems provided their chemical composition is known.

RÉSUMÉ

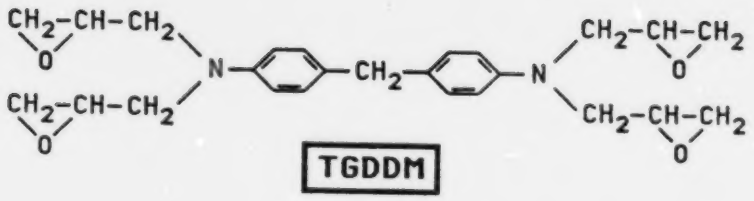
La modélisation précise du procédé de durcissement d'une résine thermodurcissable exige que l'état chimique initial de la résine soit bien connu. Dans ce travail, une méthode d'analyse des résultats obtenus par chromatographie liquide en phase inversée a été mise au point pour caractériser cet état initial dans le cas du système époxyde/amine Narmco 5208. Cette méthode a été établie en développant un modèle mathématique simplifié de la cinétique du système, ainsi qu'en préparant et analysant une série de mélanges de composition connue afin de vérifier le modèle et de déterminer les facteurs numériques nécessaires. Les deux paramètres les plus importants sont le rapport époxyde/durcisseur et le degré initial de polymérisation de la résine, qui peuvent varier d'un lot à l'autre. La méthode permet de déterminer les deux avec une bonne précision. À cause de certains problèmes reliés à la résine mineure, les teneurs individuelles des deux résines époxydes présentes sont déterminées avec une précision un peu moins bonne. Bien que les détails de la méthode soient spécifiques au Narmco 5208, les principes généraux peuvent être appliqués à d'autres systèmes pourvu que leur composition chimique soit connue.

1. INTRODUCTION

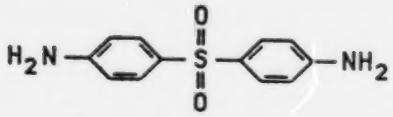
Among the most active fields in high technology today are Computer Aided Manufacturing and High-Performance Composites. A good example of the fusion of these two technologies is the computer modelling of the curing process in thermoset resins used in fibre-reinforced composites. With a good model, it is possible to predict how the system will behave during cure and what its final condition will be. In this way, the optimum curing conditions for a particular part can be determined (at least to a good approximation) without performing long and costly experimentation. The requirements of a good model have been described in recent articles [1-4]. The most important variables are temperature, degree of cure, and resin flow. In order to predict these as a function of time and position within the part, detailed information is necessary concerning the initial chemical state of the resin, the kinetics of its curing, and its rheological behaviour. Such information is not easily come by, for a number of reasons. First of all, each resin system is different and must be characterized separately. Secondly, even for a given system, batch-to-batch variations may occur, particularly with respect to the initial degree of polymerization. Thirdly, the chemistry involved in the curing process is extremely complex and virtually impossible to describe rigourously. Usually it is necessary to make a number of approximations in order to develop a usable model.

The present report describes a method which we have developed for characterizing a given lot of the Narmco Rigidite 5208 epoxy resin system. Using data obtained by physicochemical methods (mainly liquid chromatography) it is possible to determine the chemical composition, in particular the epoxy-to-hardener ratio, as well as the initial degree of polymerization or "advancement". As pointed out by Roberts [4], knowledge of these parameters is essential for accurate modelling of the cure. Although the details of the method are specific to Narmco 5208, the principles involved are applicable to other systems as well.

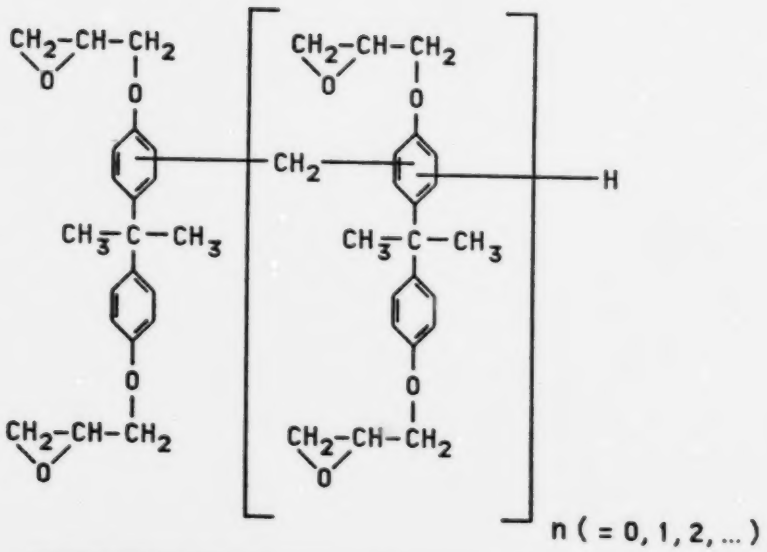
Narmco 5208 is reported to consist of two different epoxy resins and a single amine hardener [5]. The hardener is diaminodiphenylsulphone, or DDS, available commercially in relatively pure form (>98%) as Ciba-Geigy Hardener HT976. The main epoxy resin is based on tetraglycidyldiaminodiphenylmethane, or TGDDM. The commercial material, sold by Ciba-Geigy as Araldite MY720, is a complex mixture which typically contains about 68% TGDDM monomer, the rest being various oligomers and by-products [6]. The second epoxy resin present in Narmco 5208 is one based on bisphenol A Novolac. Such a product is sold by Celanese under the name Epi-Rez SU-8. Like MY720, SU-8 consists of a mixture of various components. The most easily identified is the monomer DGEBA (diglycidyl ether of bisphenol A), which accounts for about 10% of the SU-8 [6]. The chemical formulae of these materials are given in Figure 1.



TGDDM



DDS



n (= 0, 1, 2, ...)

Bisphenol A Novolac Epoxy

Fig. 1. Chemical structures of principal components of Narmco 5208 resin.

Table 1 gives the relative proportions of the two epoxy resins and the hardener, as reported by different research groups. There is significant variation among the different sets of results, and it would be desirable to have more accurate figures for use in a model of the curing process. Also, these workers did not determine the degree of advancement of the resin. Trujillo et al. reported the presence of small amounts of water (<1%) and acetone (<2%) in addition to the three main components. Acetone is used as a solvent when woven carbon-fibre fabric is impregnated with Narmco 5208.

Table 1. Composition of Narmco 5208 resin as reported by different groups.

Component	Percent by weight, as reported by:					
	Trujillo [5]	Carpenter [5,8]	Tajima* [6,7]	May [5]	Lockheed [9]	Cizmecioglu [10]
Araldite MY720	65.6	67.6	69	72.6	73	73.4
Epi-Rez SU-8	10.3	9.4	9	8.0	7	6.0
Hardener HT976	24.1	23.0	22	19.4	20	20.6

*Believed to be Narmco 5208, although not specified.

The work reported here was undertaken in order to develop a method to determine more accurately both the composition and the degree of advancement of a given batch of Narmco 5208. In previous work [11], a number of instrumental methods were developed for quality control of Narmco 5208 prepreg. These provide several parameters such as infrared spectroscopic indices and chromatographic peak ratios which can be used to monitor batch-to-batch variations in the system. However, they do not directly provide the quantities required for modelling the cure. In order to do this, it is necessary to determine the relationship between the measured quantities and the desired ones. This was done by preparing a set of mixtures of known composition, heating them for different periods of time to partially polymerize the resin, analyzing them by means of the different instrumental techniques, and finally establishing the relationship between the measured quantities and the unknown variables.

2. EXPERIMENTAL

2.1 MATERIALS

Samples of Araldite MY720 and Hardener HT976 were obtained from Ciba-Geigy, and Epi-Rez SU-8 from Celanese. Canadair supplied samples from six different batches of Narmco Rigidite 5208 prepreg, as well as two samples of neat resin, one in bulk form and one coated on a plastic backing sheet.

The epoxide content of the resins was determined by reacting the resin with excess hydrochloric acid in acetone/water solution, then titrating the excess acid with sodium hydroxide (Ciba-Geigy Test Method No. 200). The values obtained were:

Resin	Epoxy value eq/100 g	Weight per epoxide	Relative std. dev.
Araldite MY720	0.768	130.3	2.1%
Epi-Rez SU-8	0.440	227.3	0.4%

These are in good agreement with the reported typical values for these materials (weight per epoxide = 117-134 for MY720, 215 for SU-8).

For the Hardener HT976, which is near 100% pure, the equivalent weight was calculated to be 62.08, or 1.611 eq/100 g. This is based on the assumption that each molecule of DDS can react with four epoxide groups. Each of the two $-NH_2$ groups first reacts with one epoxide ring to form a secondary amine group -NH-, which can then react with a second epoxide group to form a tertiary amine group.

2.2 PREPARATION AND CHARACTERIZATION OF MIXTURES

Seven different mixtures were prepared, and the compositions are given in Table 2. Mixture #4 is based on the figures given by Tajima et al. (Table 1), which lie near the centre of the range reported. For the six others, the percentages of the different components were varied by ±9%. This gave two mixtures containing no SU-8. Mixture #5a corresponded to a repetition of #5, prepared for reasons to be discussed later. The quantities "f" and "g" are an alternative way of defining the composition. They correspond to the epoxide/amine equivalent ratio for MY720 and SU-8 respectively, and are calculated as follows, based on the results given in Section 2.1:

$$f = \frac{(\%\ \mathrm{MY720}) \times 0.768}{(\%\ \mathrm{HT976}) \times 1.611} \qquad (1)$$

$$g = \frac{(\%\ SU{-}8) \times 0.440}{(\%\ HT976) \times 1.611} \qquad (2)$$

The sum f + g is equal to the total epoxide-to-amine ratio, and has a value of 1 for a stoichiometric mixture. In mixture #4, corresponding to the expected composition of Narmco 5208, the ratio is 1.6. In this case, the excess epoxide groups are polymerized by reaction with OH groups and with each other to give ether linkages.

Table 2 Compositions of the different mixtures prepared.

Mixture	% HT976	% MY720	% SU-8	f	g	f+g
1	22.27	59.73	18.00	1.279	0.221	1.500
2	13.13	68.80	18.08	2.498	0.376	2.874
3	31.54	59.49	8.97	0.899	0.078	0.977
4	22.05	68.92	9.03	1.490	0.112	1.602
5	13.17	77.78	9.05	2.816	0.188	3.004
6	31.01	68.99	0.00	1.061	0.0	1.061
7	22.03	77.97	0.00	1.687	0.0	1.687
5a	13.45	77.23	9.32	2.737	0.189	2.926

For each mixture, precisely weighed quantities of MY720, SU-8, and HT976 were combined (to give a total weight of about 10 g) and dissolved in reagent grade acetone. The solution was then divided equally among ten aluminum weighing dishes and the acetone allowed to evaporate. To remove as much of the acetone as possible without heating the mixtures, they were left under vacuum overnight. Four of the dishes were left unheated, and the remaining six were placed in an air-circulating oven at 120°C to partially polymerize the mixture. Three were removed after 30 minutes, which was judged from preliminary trials to be sufficient to give a product equivalent to typical B-staged Narmco 5208. The remaining three were left for 80 minutes (95 minutes in the case of mixture #1) in order to give a somewhat overstaged product. This gave a total of 21 samples (7 compositions x 3 degrees of polymerization) which were analyzed by liquid chromatography, Fourier transform infrared spectroscopy, and thermal analysis, using methods given in detail in a previous report [11]. Of each set of three specimens, one was used for each technique mentioned.

3. RESULTS AND DISCUSSION

3.1 THERMAL ANALYSIS

The enthalpy of polymerization of each sample was measured by differential scanning calorimetry (DSC) in a nitrogen atmosphere at a heating rate of 5°C/min. A precisely weighed quantity of resin (about 50 mg) was placed in a platinum crucible and run against an empty matched crucible as reference. The DSC curves show a single exothermic peak lying between 200 and 300°C. The area under the peak was calculated with respect to a baseline drawn from valley to valley, converted to joules, and divided by the weight of resin to obtain ΔH in joules per gram of resin. For each sample, three specimens were analyzed and averaged to give the results shown in Table 3.

Table 3. Thermal analysis results: Enthalpy of polymerization ΔH (J/g), standard deviation in parentheses.

Mixture	Heating Time at 120°C					
	0 min		30 min		80 min†	
1	565.6	(7.8)	577.2	(4.1)	543.6	(3.1)
2	623.5	(3.0)	633.4	(4.2)	630.0	(6.4)
3	533.3	(4.6)	526.4	(1.0)	479.3	(2.8)
4	595.7	(4.1)	608.0	(2.8)	579.3	(5.9)
5	657.5	(4.8)	674.5	(1.0)	672.5	(3.8)
6	563.3	(3.7)	560.0	(4.2)	518.2	(2.6)
7	643.7	(5.4)	651.5	(7.0)	634.0	(1.9)

†95 min for Mixture 1

The variation of ΔH with heating time is illustrated graphically in Figure 2. An unusual behaviour is observed. Instead of the expected decrease with heating time, as the resin becomes more and more polymerized, in most cases the unheated sample has a lower ΔH than the one heated for 30 minutes. The reason for this is believed to be residual acetone in the unheated samples. Although the DSC curves did not show an endothermic peak corresponding to acetone evaporation, it appears that a small amount is nevertheless present. As a result, the sample weight used in calculating ΔH for $t = 0$ is somewhat higher than the true resin weight, and this results in an artificially low value for ΔH. If we estimate the true value of ΔH_0 by a linear extrapolation of the values for 30 min and 80 min, the deviations between the estimated true value and the measured value range from 2 to 5 %. The problem of residual acetone is difficult to overcome, since heating the resin to

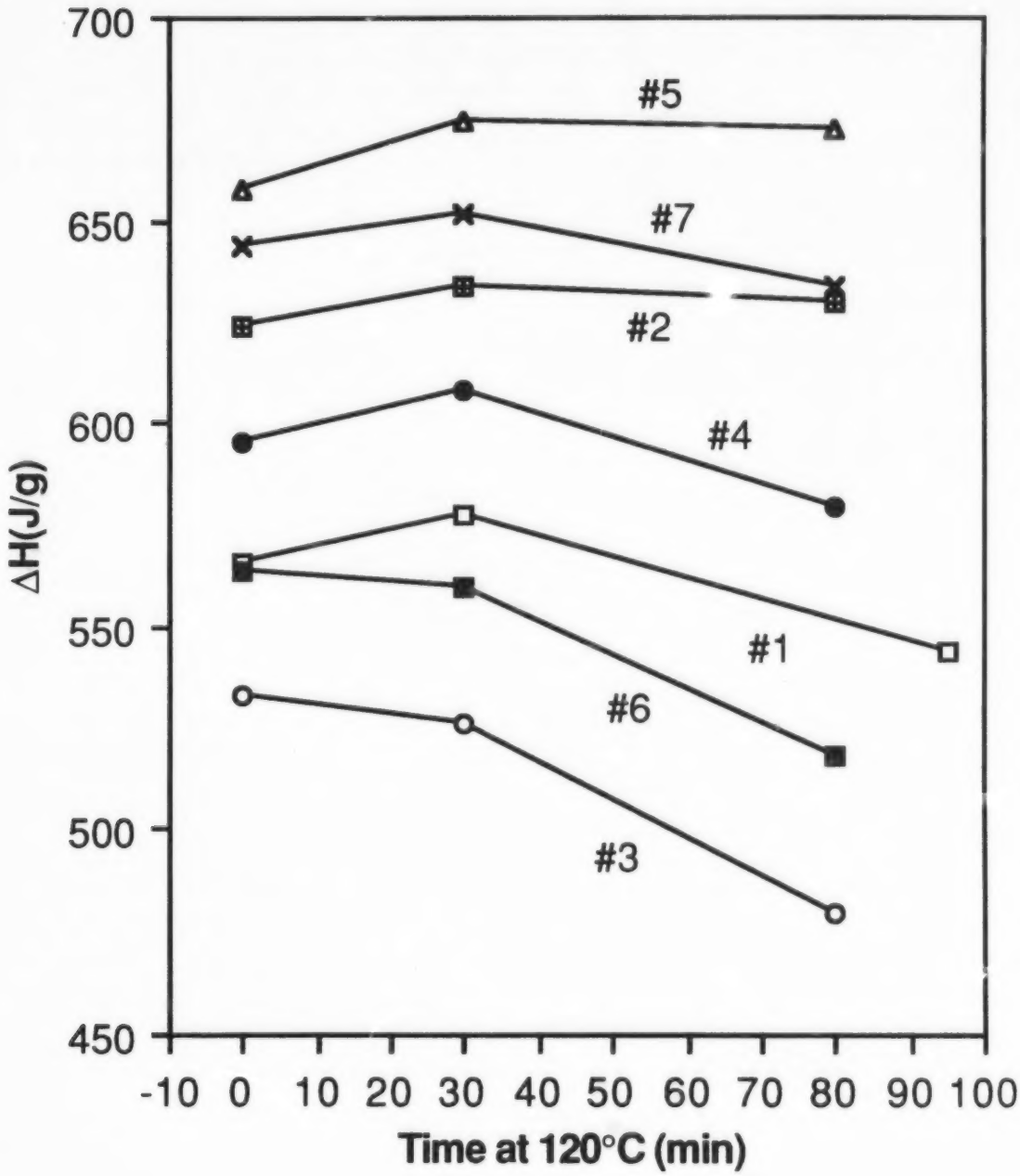


Fig. 2. Relationship between enthalpy of polymerization ΔH, as measured by DSC, and heating time at 120°C for the different mixtures.

remove all the acetone would promote polymerization, probably causing an error as great as that caused by the acetone. This error is not particularly large, for general purposes, but it becomes important if the ΔH values are used to calculate a value for α, the degree of polymerization. This is done using the following equation:

$$\alpha = \frac{\Delta H_0 - \Delta H_t}{\Delta H_0} \qquad (3)$$

Since α is related to a small difference between two larger quantities, the relative error is considerably amplified. In fact, the values of α for t = 30 min would in most cases be negative, which is physically meaningless.

The values of ΔH for 30 min and 80 min are believed to be more accurate, because the residual acetone would have evaporated during the heating. In all cases, ΔH drops on going from 30 min to 80 min, but the magnitude of the drop depends on the mixture. It is very small for mixtures #2 and #5, somewhat higher for mixtures #1, #4, and #7, and higher still for mixtures #3 and #6. This reflects the hardener content of these three groups, which is 13%, 22%, and 31% respectively. Thus, the higher the HT976 content, the more epoxy groups react when heated for the specified time.

In the case of the unheated mixtures, the epoxide content is well defined, and it is possible to calculate the enthalpy of polymerization per epoxide group present. This gives the following results:

Table 4. Enthalpy of polymerization per epoxide group.

Mixture	ΔH per epoxide group (kJ/mol)
1	105.2
2	102.6
3	107.4
4	104.7
5	103.2
6	106.3
7	107.5

It is seen that the ΔH values per epoxide group are very similar for all seven mixtures, although #2 and #5 appear to give slightly lower values than the others. This could be because these two have a very high epoxide-to-amine ratio, and some of the epoxide

groups may remain unreacted under the conditions of the DSC experiment. Omitting these two mixtures, the average value for the other five is 106.2 kJ/mol. For the mixtures containing only MY720 and HT976 (#6 and #7), the results are in excellent agreement with those reported by Barton [12]. The fact that ΔH per epoxide group is practically constant for the seven mixtures underlines the following points, important for the cure modelling of Narmco 5208:

(i) ΔH per epoxide group for the epoxide-OH reaction is similar to that for the epoxide-amine reaction; otherwise different values would be obtained for mixture #6 (epoxide-to-amine ratio = 1.1) and mixture #7 (epoxide-to-amine ratio = 1.7).

(ii) ΔH per epoxide group for Epi-Rez SU-8 is similar to that for Araldite MY720; otherwise different values would be obtained for mixture #7, with no SU-8, and mixture #1, in which 15% of the epoxide groups originate from SU-8.

The temperature corresponding to the peak maximum in the DSC curve was also recorded, and the values are given in Table 5.

Table 5. Thermal analysis results: T_{max} (°C)

Mixture	Heating Time at 120°C		
	0 min	30 min	80 min†
1	248	247	248
2	268	267	268
3	217	215	213
4	250	250	249
5	267	267	267
6	220	217	217
7	252	252	252

†95 min for Mixture 1

It can be seen that T_{max} is not significantly affected by the degree of advancement (within the range studied) but is quite sensitive to the mixture composition, in particular the percentage of HT976. As the latter increases, the maximum in the DSC curve moves to lower temperature. Figure 3 shows the relation graphically, together with a second-order polynomial fit. Carpenter [8] has observed a similar relationship and used a logarithmic inverse-temperature equation to fit the data.

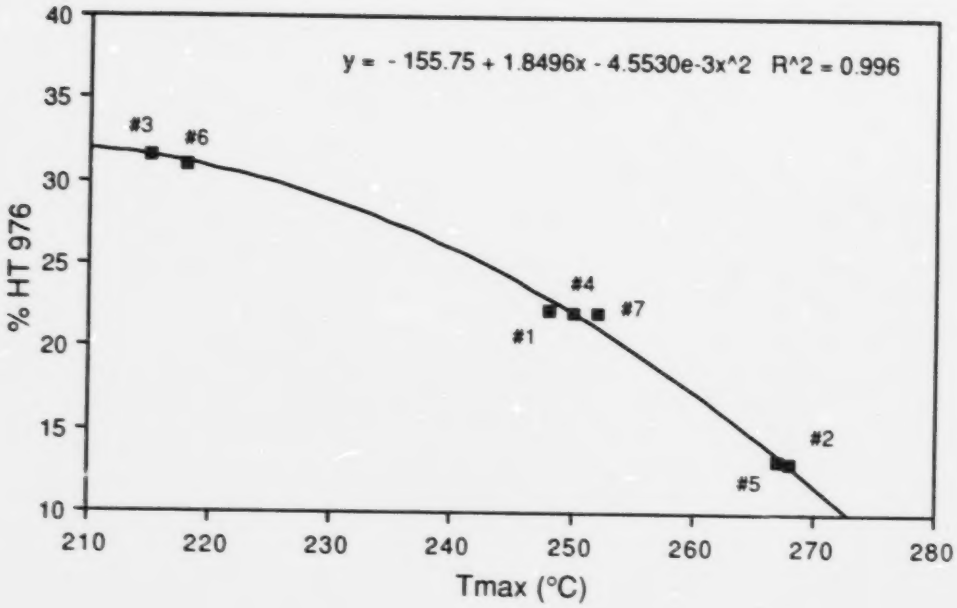


Figure 3. Relationship between HT976 content and temperature at which maximum occurs in the DSC curve.

3.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

The 21 mixtures were analyzed as thin cast films by transmission FT-IR, using the method described in an earlier report [11]. Two indices were calculated: the sulphone index and the epoxide index. Unfortunately, upon analysis of the data, some of the results were found to have unacceptably high standard deviations. This is believed to be because of a high humidity level in the laboratory, which resulted in moisture condensation on the windows when the solvent was evaporated. These samples would have to be repeated in order to obtain usable results. The remaining results are shown in Table 6 (sulphone index) and Table 7 (epoxide index). Each result is an average over three to five specimens, with the standard deviation shown in parentheses.

The sulphone index is the ratio of the area of the DDS sulphone bands at 1150-1100 cm^{-1} with respect to the aromatic ring band at 1517 cm^{-1}. The latter arises mainly from the epoxy resins present, so the sulphone index is quite sensitive to the ratio of hardener to epoxy. However, since the sulphone groups remain intact on polymerization, the index is not very much affected by the heating of the resin. This is confirmed by the results shown in Table 6. If we take the average of the three results for each mixture and plot this against

the percentage of HT976, the graph shown in Figure 4 is obtained. There is a good linear relationship described by the equation:

$$\%\text{HT976} = 23.7 \times (\text{Sulphone Index}) - 2.5 \quad (4)$$

Table 6. FT-IR results for the sulphone index; standard deviations shown in parentheses.

Mixture	Heating Time at 120°C					
	0 min		30 min		80 min†	
1	1.085	(0.017)	1.083	(0.010)	1.124	(0.023)
2	0.686	(0.009)	0.681	(0.003)	0.687	(0.002)
3	--		--		--	
4	0.997	(0.013)	1.016	(0.020)	1.046	(0.007)
5	--		0.641	(0.004)	--	
6	--		--		1.405	(0.013)
7	0.986	(0.009)	1.021	(0.003)	1.003	(0.008)

†95 min for Mixture 1

Table 7. FT-IR results for the epoxide index; standard deviations shown in parentheses.

Mixture	Heating Time at 120°C					
	0 min		30 min		80 min†	
1	0.403	(0.006)	0.384	(0.004)	0.368	(0.007)
2	0.427	(0.005)	0.420	(0.003)	0.411	(0.002)
3	--		--		--	
4	0.397	(0.002)	0.399	(0.007)	0.384	(0.009)
5	--		0.436	(0.006)	--	
6	--		--		0.373	(0.001)
7	0.451	(0.007)	0.436	(0.002)	0.421	(0.010)

†95 min for Mixture 1

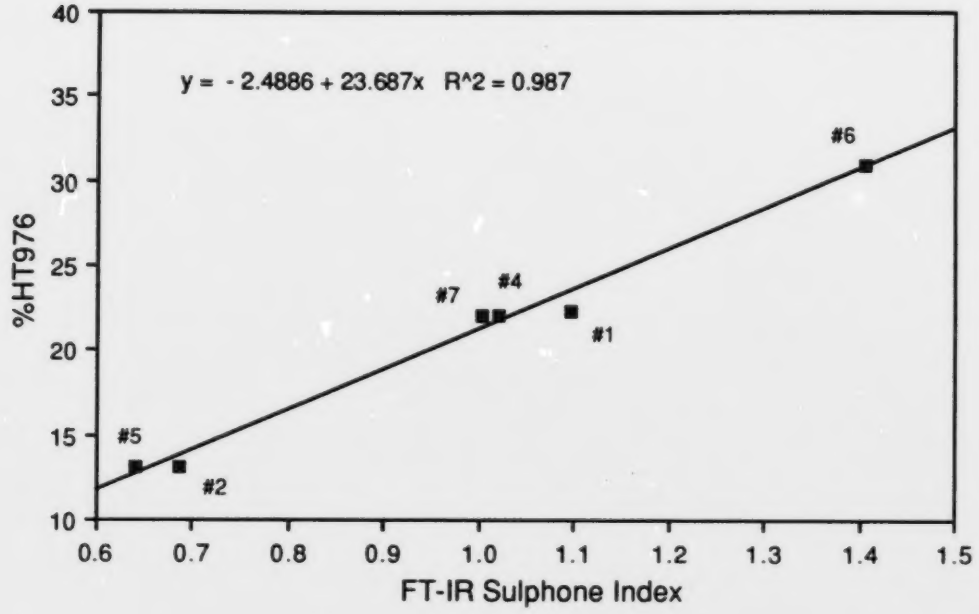


Figure 4. Relationship between HT 976 content and FT-IR sulphone index.

The epoxide index is the ratio of the epoxide peaks at 1000-900 cm^{-1} with respect to the aromatic ring peak. Since both arise primarily from the epoxy resin, this index is not very sensitive to the hardener/epoxy ratio. However, because the peaks at 1000-900 cm^{-1} are due to epoxide rings, which disappear on reaction with the hardener, this index should decrease when the resin is heated. This is confirmed by the results shown in Table 7 and Figure 5. In theory, the epoxide index (EI) can be used to estimate α according to the following equation, similar to that used for the enthalpy of polymerization (Eq. 3):

$$\alpha = \frac{EI_0 - EI_t}{EI_0} \qquad (5)$$

However, as in the enthalpy case, the error will be relatively large, because α is calculated as a small difference between two larger quantities.

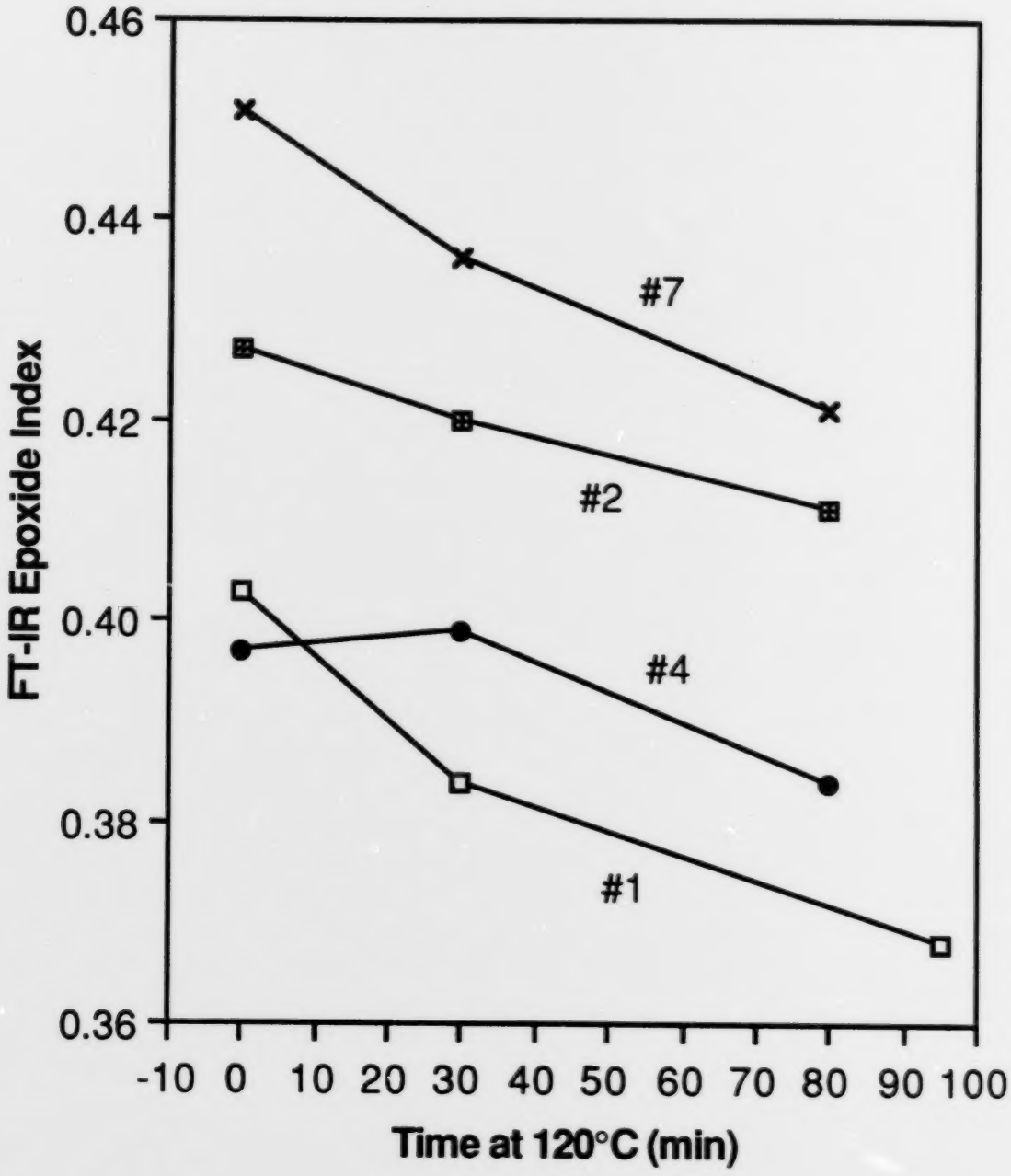


Fig. 5. Relationship between FT-IR epoxide index and heating time at 120°C for certain mixtures.

3.3 REVERSE-PHASE LIQUID CHROMATOGRAPHY (RPLC)

The method used for the reverse-phase liquid chromatography analysis is also given in an earlier report [11]. The resin is dissolved in tetrahydrofuran, acetophenone is added as an internal standard, and the components are separated by gradient elution using a mixture of acetonitrile and water as eluent. The areas of peaks corresponding to the following five main components are measured:

(i) DDS = diaminodiphenylsulphone (from the hardener HT976);

(ii) TGDDM = tetraglycidyldiaminodiphenylmethane (from the main epoxy MY720);

(iii) DGEBA = diglycidyl ether of bisphenol A (from the minor epoxy SU-8);

(iv) RP = reaction product (1:1) formed from TGDDM and DDS;

(v) ACP = acetophenone (internal standard).

Using the acetophenone peak as a reference, it is possible to calculate a normalized peak area for each of the other peaks. This quantity is directly proportional to the percentage by weight of the particular component in the resin sample. The results obtained for the four main peaks in the 21 samples analyzed are given in Tables 8 to 11. Each result is an average over three injections made from the same solution; the standard deviations are given in parentheses. The results are also illustrated graphically in Figures 6 to 9.

Table 8. RPLC results for the DDS peak (normalized area); standard deviation shown in parentheses.

Mixture	Heating Time at 120°C					
	0 min		30 min		80 min†	
1	5.656	(0.085)	5.257	(0.020)	3.709	(0.018)
2	3.348	(0.020)	3.041	(0.044)	2.580	(0.007)
3	7.551	(0.053)	6.818	(0.020)	5.028	(0.057)
4	5.536	(0.038)	5.069	(0.071)	4.166	(0.017)
5	3.303	(0.099)	3.271	(0.054)	2.790	(0.009)
6	7.622	(0.044)	7.047	(0.006)	5.672	(0.020)
7	5.621	(0.122)	5.306	(0.033)	4.566	(0.062)
5a	3.314	(0.023)	3.237	(0.057)	2.670	(0.046)

†95 min for Mixture 1

Table 9. RPLC results for the TGDDM peak (normalized area); standard deviation shown in parentheses.

Mixture	Heating Time at 120°C					
	0 min		30 min		80 min†	
1	12.454	(0.075)	12.240	(0.009)	10.853	(0.068)
2	14.271	(0.053)	13.966	(0.095)	13.595	(0.003)
3	11.750	(0.114)	10.874	(0.059)	9.438	(0.130)
4	14.137	(0.048)	13.588	(0.207)	12.825	(0.026)
5	15.218	(0.784)	16.219	(0.306)	15.763	(0.011)
6	13.787	(0.038)	13.158	(0.148)	11.552	(0.213)
7	15.999	(0.261)	15.606	(0.042)	14.601	(0.205)
5a	14.989	(0.125)	15.458	(0.121)	14.473	(0.224)

†95 min for Mixture 1

Table 10. RPLC results for the DGEBA peak (normalized area); standard deviation shown in parentheses.

Mixture	Heating Time at 120°C					
	0 min		30 min		80 min†	
1	1.815	(0.038)	1.837	(0.005)	1.717	(0.009)
2	1.908	(0.112)	2.030	(0.011)	1.997	(0.022)
3	0.971	(0.010)	0.902	(0.049)	0.981	(0.016)
4	0.887	(0.015)	0.928	(0.047)	0.937	(0.022)
5	1.003	(0.039)	0.997	(0.027)	0.955	(0.020)
6	0.097	(0.003)	0.313	(0.003)	0.549	(0.028)
7	0.043	(0.004)	0.125	(0.007)	0.256	(0.018)
5a	0.875	(0.003)	0.980	(0.008)	0.971	(0.002)

†95 min for Mixture 1

Table 11. RPLC results for the RP peak (normalized area); standard deviation shown in parentheses.

Mixture	Heating Time at 120°C		
	0 min	30 min	80 min†
1	0.039 (0.002)	0.639 (0.004)	1.795 (0.009)
2	0.000 (0.000)	0.381 (0.001)	0.796 (0.003)
3	0.069 (0.004)	1.050 (0.013)	2.324 (0.015)
4	0.010 (0.001)	0.596 (0.023)	1.493 (0.010)
5	0.000 (0.000)	0.359 (0.012)	0.810 (0.004)
6	0.084 (0.001)	1.451 (0.013)	2.619 (0.041)
7	0.000 (0.000)	0.556 (0.009)	1.556 (0.034)
5a	0.012 (0.002)	0.333 (0.014)	0.804 (0.004)

†95 min for Mixture 1

Figure 6 shows the variation in the quantity of free DDS for the seven different mixtures as a function of the heating time at 120°C. As expected, it decreases with heating time, the rate being higher for the mixtures containing more HT976. In some cases, the decrease is more-or-less linear with time, but in others there is an apparent downward curvature, and in one (#5), the 0 and 30 min values are approximately the same. These effects could be due to residual acetone in the resin. Since the weight of resin is used in calculating the normalized area, residual acetone will cause a systematic error in the same way as described for the enthalpy of polymerization ΔH.

Figure 7 shows the results for TGDDM. They show the same trends as DDS, although the decrease is not as pronounced. Again, unusual behaviour is observed for mixture #5.

In Figure 8, the DGEBA behaviour is plotted, and it is found to be different from what is expected. Mixtures 6 and 7, which contain no SU-8, should not give a DGEBA peak. This is true for the unheated samples (to a good approximation), but not for the heated ones. It appears that MY720 and HT976 give a reaction product (other than RP) which elutes at the same retention time as the DGEBA. As a result, in the mixtures containing SU-8, where the DGEBA peak is expected to diminish with heating, it remains approximately constant, because as the DGEBA disappears it is replaced by the unidentified reaction product. This must be taken into account in any analysis method making use of the DGEBA peak.

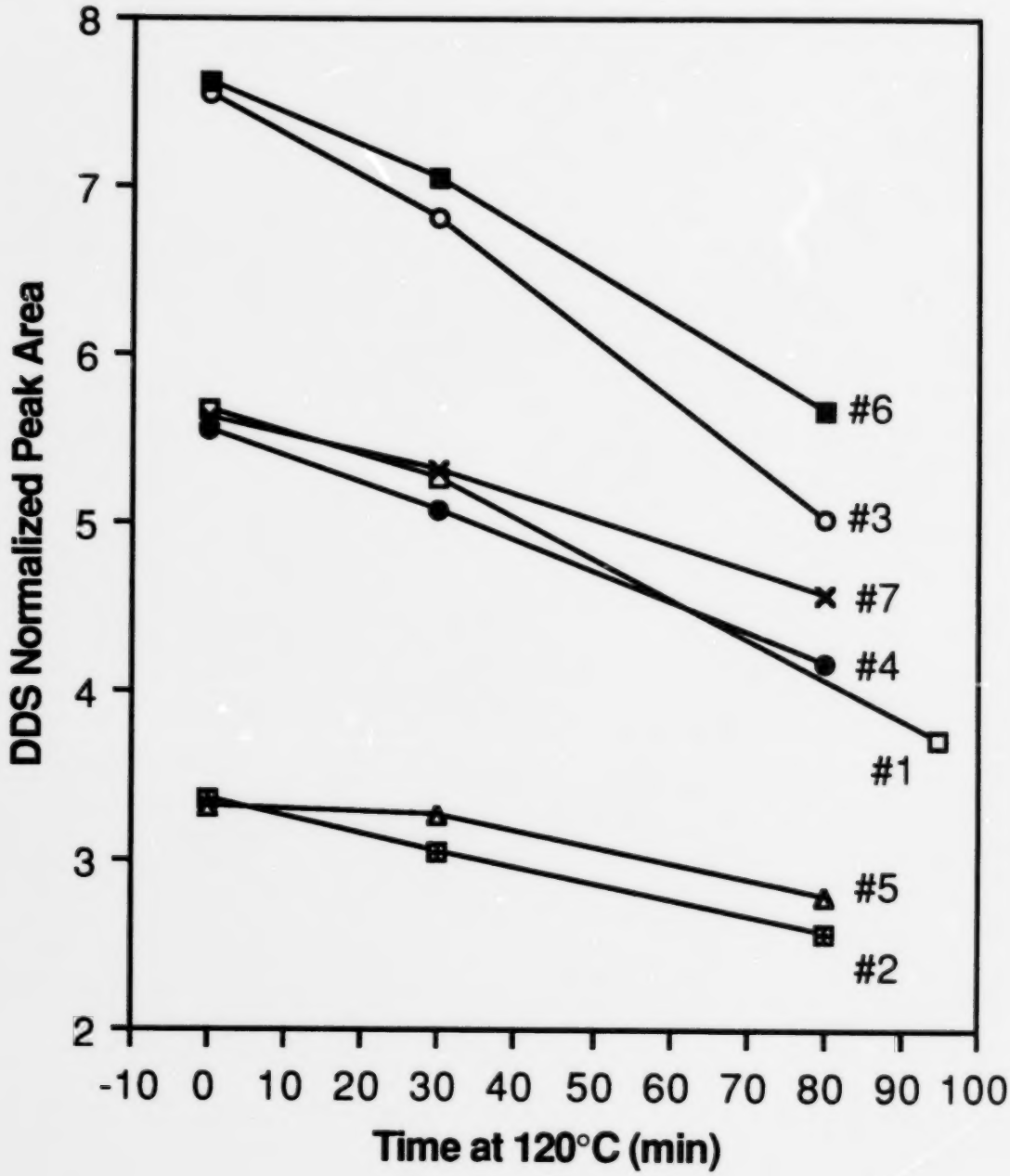


Fig. 6. Relationship between normalized area of the DDS peak, as determined by RPLC, and heating time at 120°C for the different mixtures.

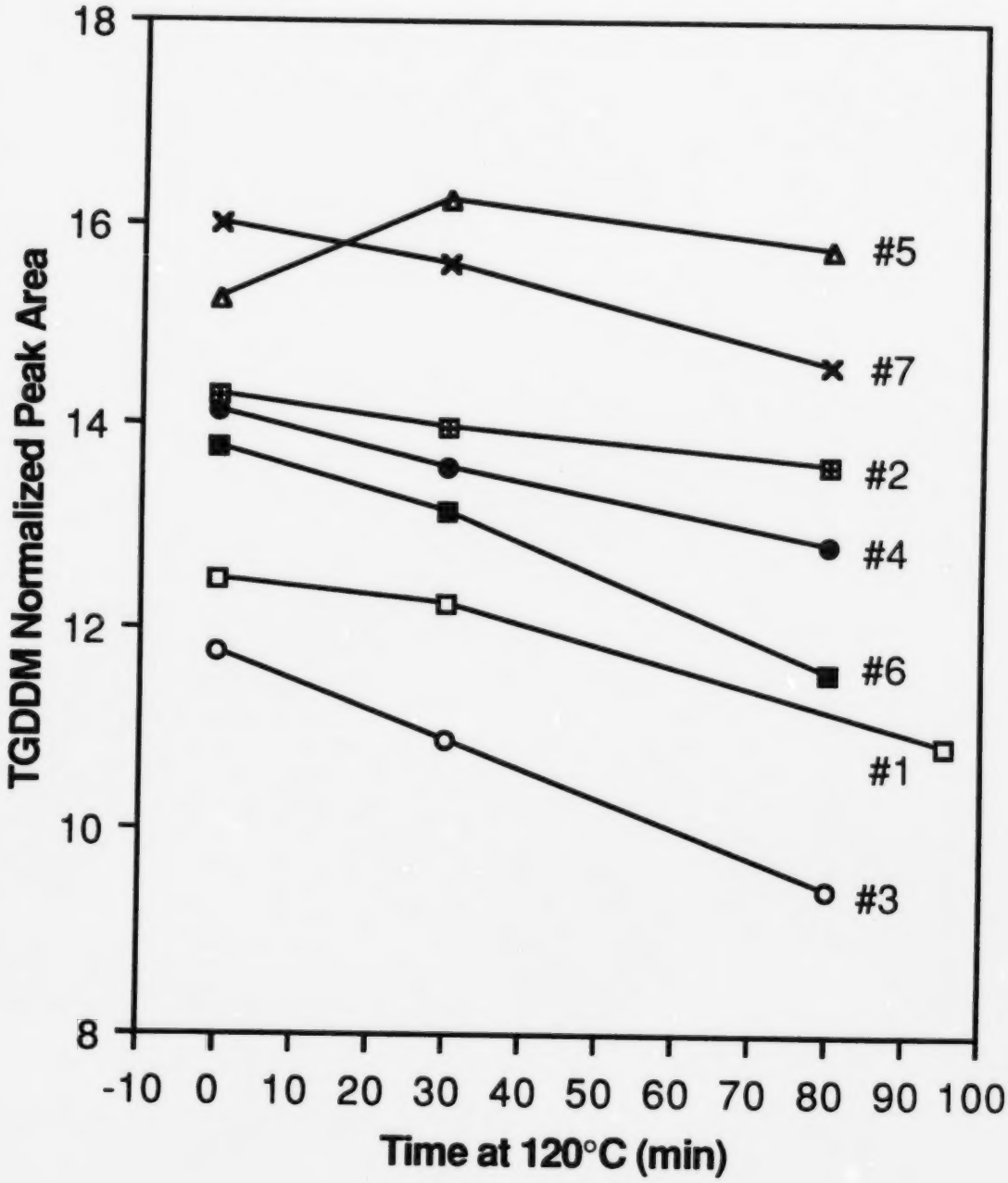


Fig. 7. Relationship between normalized area of the TGDDM peak, as determined by RPLC, and heating time at 120°C for the different mixtures.

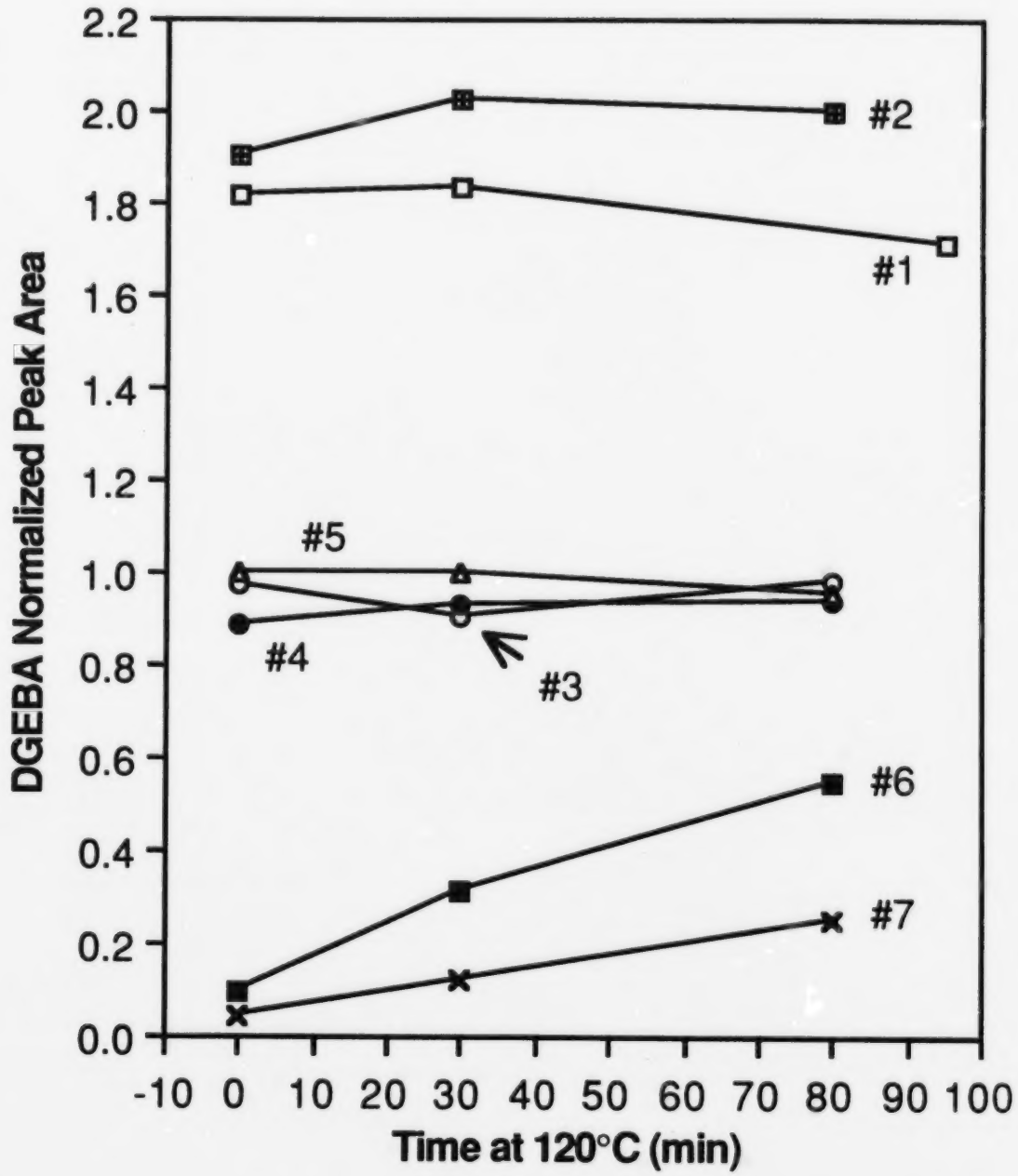


Fig. 8. Relationship between normalized area of the DGEBA peak, as determined by RPLC, and heating time at 120°C for the different mixtures.

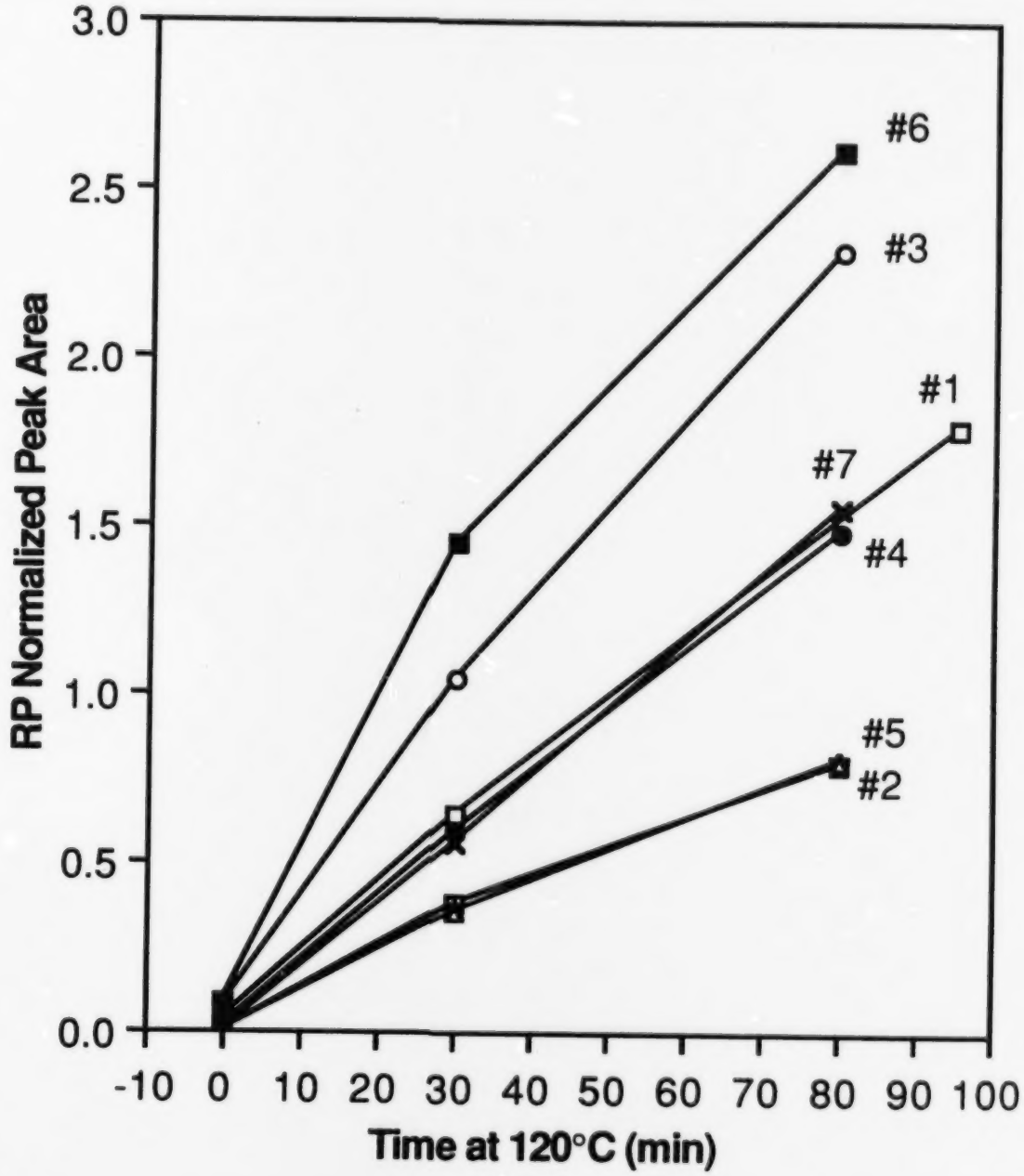


Fig. 9. Relationship between normalized area of the RP (TGDDM-DDS reaction product) peak, as determined by RPLC, and heating time at 120°C for the different mixtures.

Finally, Figure 9 shows the results for the main reaction product peak (RP). As anticipated, the amount increases substantially on heating and the rate of increase is highly dependent on the amount of HT976 in the mixture.

Because of the unusual results obtained for mixture #5, the experiment was repeated, and the results are given as mixture #5a in the tables. Unfortunately, the same type of behaviour was observed. It appears that this mixture strongly retains acetone.

One way of overcoming the problems with residual acetone is to use ratios of areas of peaks arising from the resin only. In this way, the weights of the resin and acetophenone do not enter into the calculation, so two possible sources of error are eliminated. As will become evident later, it is advisable to take the DDS peak as a reference for calculating the ratios. The results are given in Tables 12 to 14 and Figures 10 to 12.

It can be seen that the unusual behaviour associated with mixture #5 is no longer evident, and in most cases, the variation with heating time is not too far from linear. Both TGDDM and DDS decrease with heating, but the DDS decreases faster, so the ratio shows a gradual increase. The same is true for DGEBA, which, as pointed out above, is complicated by interference from one of the reaction products. The RP/DDS ratio, on the other hand, shows a drastic change with heating, because while DDS is disappearing, RP is being formed.

Table 12. RPLC results for the TGDDM/DDS peak area ratio.

Mixture	Heating Time at 120°C					
	0 min		30 min		80 min†	
1	2.2023	(0.0226)	2.3282	(0.0071)	2.9261	(0.0242)
2	4.2626	(0.0318)	4.5930	(0.0443)	5.2685	(0.0127)
3	1.5559	(0.0058)	1.5948	(0.0081)	1.8773	(0.0070)
4	2.5534	(0.0168)	2.6803	(0.0131)	3.0788	(0.0116)
5	4.6041	(0.0994)	4.9589	(0.0148)	5.6492	(0.0144)
6	1.8090	(0.0055)	1.8670	(0.0224)	2.0362	(0.0388)
7	2.8463	(0.0274)	2.9410	(0.0254)	3.1976	(0.0149)
5a	4.5225	(0.0065)	4.7754	(0.0467)	5.4201	(0.0103)

†95 min for Mixture 1

Table 13. RPLC results for the DGEBA/DDS peak area ratio.

Mixture	Heating Time at 120°C					
	0 min		30 min		80 min†	
1	0.3209	(0.0059)	0.3495	(0.0015)	0.4630	(0.0040)
2	0.5700	(0.0340)	0.6677	(0.0072)	0.7738	(0.0089)
3	0.1286	(0.0006)	0.1323	(0.0078)	0.1952	(0.0047)
4	0.1602	(0.0030)	0.1830	(0.0065)	0.2250	(0.0055)
5	0.3042	(0.0283)	0.3049	(0.0027)	0.3421	(0.0071)
6	0.0127	(0.0003)	0.0444	(0.0006)	0.0968	(0.0061)
7	0.0077	(0.0006)	0.0235	(0.0015)	0.0560	(0.0035)
5a	0.2640	(0.0014)	0.3027	(0.0030)	0.3637	(0.0063)

†95 min for Mixture 1

Table 14. RPLC results for the RP/DDS peak area ratio.

Mixture	Heating Time at 120°C					
	0 min		30 min		80 min†	
1	0.0069	(0.0003)	0.1215	(0.0008)	0.4839	(0.0047)
2	0.0000	(0.0000)	0.1255	(0.0014)	0.3086	(0.0015)
3	0.0091	(0.0005)	0.1540	(0.0014)	0.4623	(0.0058)
4	0.0018	(0.0002)	0.1176	(0.0028)	0.3583	(0.0022)
5	0.0000	(0.0000)	0.1097	(0.0019)	0.2904	(0.0015)
6	0.0110	(0.0001)	0.2059	(0.0026)	0.4616	(0.0089)
7	0.0000	(0.0000)	0.1048	(0.0017)	0.3408	(0.0031)
5a	0.0038	(0.0006)	0.1028	(0.0035)	0.3008	(0.0032)

†95 min for Mixture 1

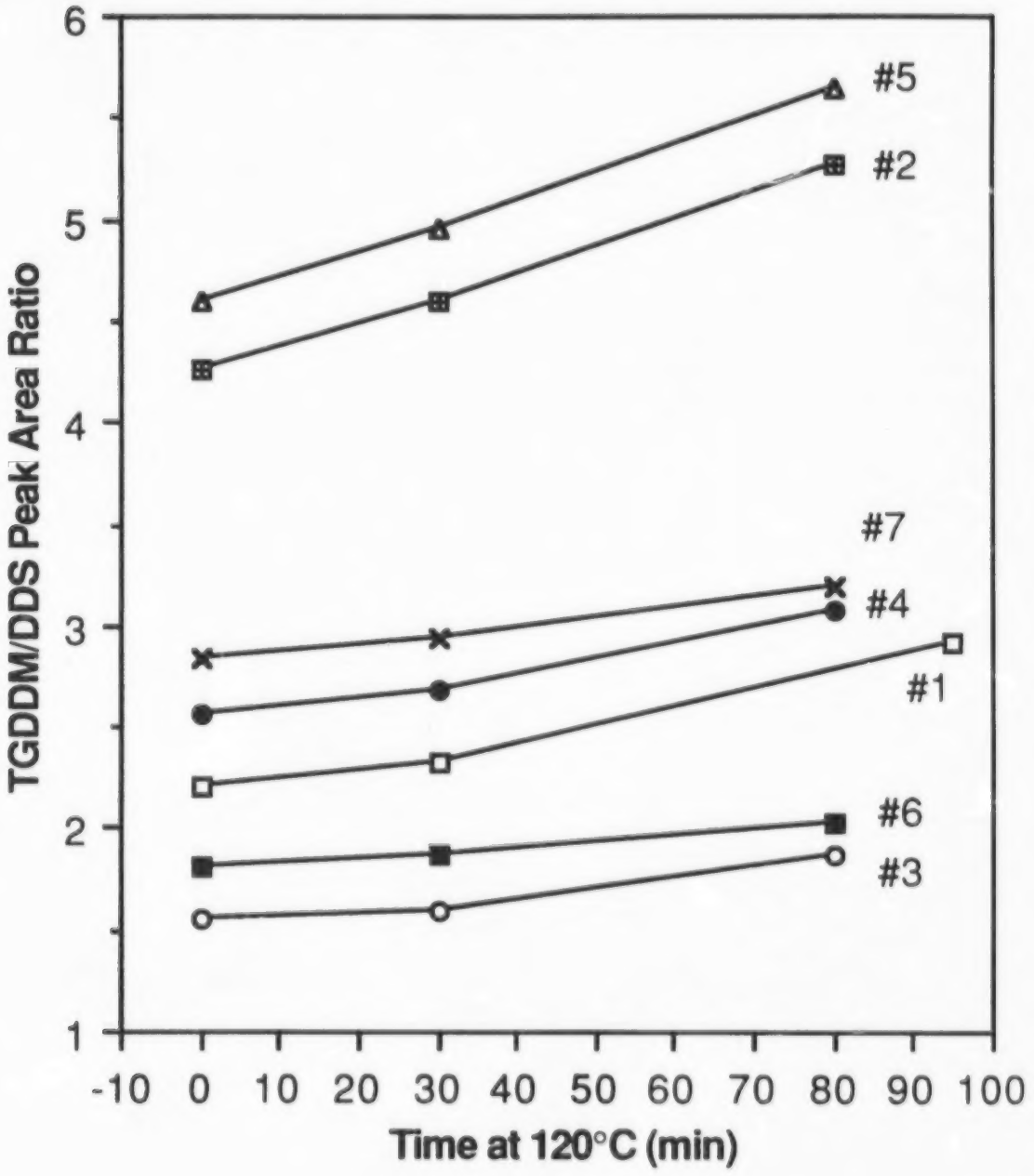


Fig. 10. Relationship between the TGDDM/DDS peak area ratio and heating time at 120°C for the different mixtures.

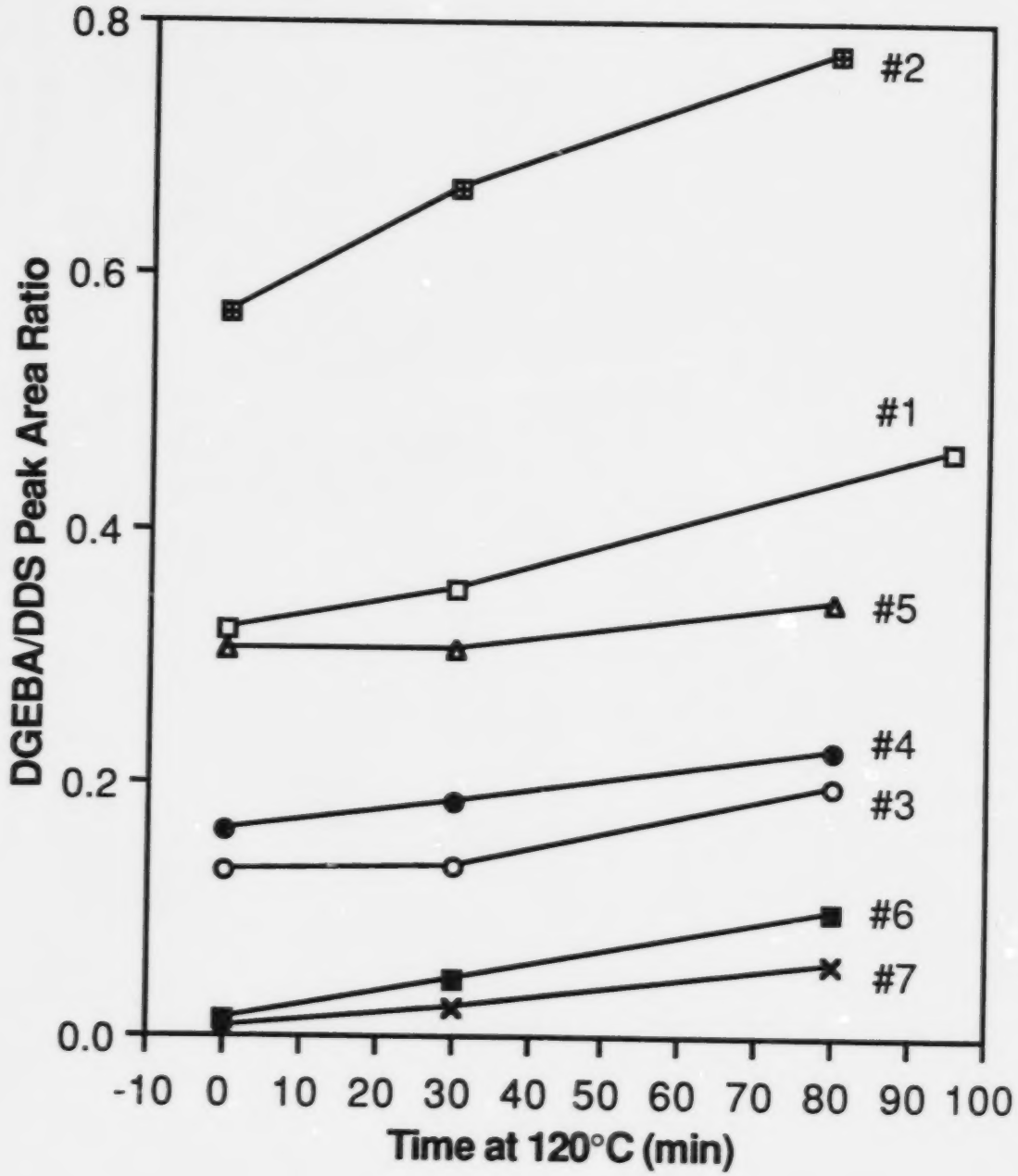


Fig. 11. Relationship between the DGEBA/DDS peak area ratio and heating time at 120°C for the different mixtures.

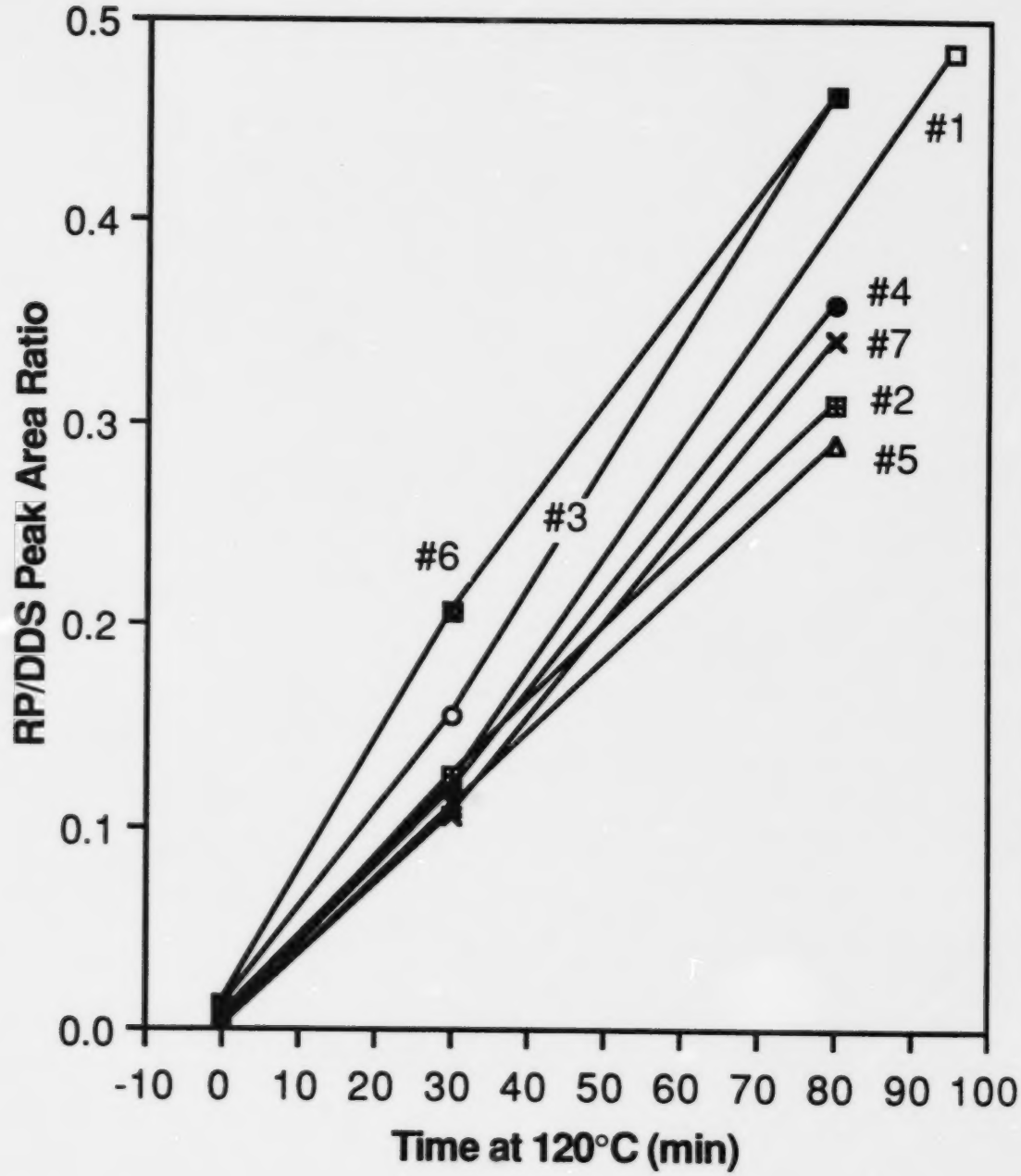


Fig. 12. Relationship between the RP/DDS peak area ratio and heating time at 120°C for the different mixtures.

3.4 TREATMENT OF THE RPLC RESULTS

It is seen that liquid chromatography provides more data, and more precise data, than do thermal analysis or FT-IR, at least using the methods employed in this work. It remains to determine the best way of extracting the desired information from the LC data. In effect, LC gives three known quantities (the three peak area ratios TGDDM/DDS, DGEBA/DDS, and RP/DDS) which are closely related to the three unknown quantities required to define the resin (f, g, and α). The quantities f and g are directly related to the percentages of the three components used in making the resin, whereas α is a quantitative measure of the degree of polymerization. The problem to be solved consists in determining the rather complex relationship between the known and the unknown quantities, since all three peak ratios vary with α and the variation depends on the particular values of f and g. To overcome this problem, the kinetics of the reaction were analyzed as described in Appendix A. This simplified model considers the reaction of DDS (labelled **A**) with two monofunctional epoxy resins of different reactivity (**B** and **B′**). The respective epoxide-to-amine ratios are f and g, and the initial reaction products are labelled **C** and **C′** respectively. Because of the complexity of the system, certain simplifications are necessary, and even then, an exact solution is possible only for the concentration of DDS. For the others, the results are expressed as series in α. Since we are interested only in the very first stages of the reaction, where α is small, it should be possible to achieve good results using only the first-order term in α. For the same reason, the model considers only the epoxide-amine reaction and neglects the epoxide-hydroxyl reaction which takes place mainly at a later stage. This model (Appendix A) leads to the following equations for the concentrations of the main components of interest:

$$A = A_0[1-(f+g)\alpha]^4 \tag{6}$$

$$B \approx 4fA_0\left[1-\frac{f+g}{f+rg}\alpha\right] \tag{7}$$

$$B' \approx 4gA_0\left[1-r\frac{f+g}{f+rg}\alpha\right] \tag{8}$$

$$C \approx 4fA_0\left[\frac{f+g}{f+rg}\alpha\right] \tag{9}$$

$$C' \approx 4rgA_0\left[\frac{f+g}{f+rg}\alpha\right] \tag{10}$$

In these equations, A_0 represents the concentration of **A** (DDS) in the unreacted mixture (i.e. when $\alpha = 0$); A, B, B', C, and C' are the concentrations of the respective components in the partially reacted mixture; and r is a coefficient expressing the reactivity of the minor epoxy **B'** relative to that of the major epoxy **B** (see Appendix A).

To apply this model, it is first of all necessary to define α for the mixtures used for the "calibration". As pointed out previously, this can be done using thermal analysis or FT-IR results, but this gives rise to significant errors. An alternative possibility is to use the RPLC results. By inverting Equation 6 we obtain:

$$\alpha = \frac{1}{f + g}\left[1 - \left(\frac{A}{A_0}\right)^{0.25}\right] \qquad (11)$$

This equation can be used to determine α from the values for the normalized DDS peak area (Table 8), which are proportional to A. Because of the nature of Equation 6, A decreases at a much faster rate with respect to α than does the total number of epoxide groups measured by DSC or FT-IR. For example, taking the case where $f + g = 1.6$, at the stage when 10% of the epoxide groups have reacted ($\alpha = 0.1$), 50% of the free DDS has disappeared! Thus, the DDS peak area is much more sensitive to variations in α than are the heat of polymerization determined by DSC or the epoxide index determined by FT-IR. As a result, the α determined according to Equation 11 is less affected by experimental error than α determined by the other methods. Nevertheless, some error, including that caused by residual acetone in the samples, is still present.

Table 15 shows the values of α determined as just described, based on the data in Table 8. In the case of Mixture #5, the initial value for the DDS peak is believed to be considerably affected by the presence of acetone, as discussed previously. Hence a "corrected" value of 3.560, obtained by linear extrapolation of the values corresponding to 30 and 80 min heating (see Figure 6), was used for the calculation. The standard deviations given in the table were calculated from the data in Table 8 using standard "propagation of error" procedures.

Table 16 compares the third column of Table 15 with values obtained for the same mixtures by DSC (calculated from Table 3 using Equation 3) and FT-IR (calculated from Table 7 using Equation 5). Considering the significant errors involved in the DSC and FT-IR results, there is reasonable agreement among the three methods. However, it is obvious that the RPLC results are subject to a much smaller propagation of error and are therefore preferred, even though they are calculated by a somewhat less direct procedure.

Table 15. Values of α calculated using the RPLC results for the DDS peak.

Mixture	Heating Time at 120°C				
	0 min	30 min		80 min†	
1	0	0.0121	(0.0025)	0.0667	(0.0024)
2	0	0.0083	(0.0013)	0.0219	(0.0005)
3	0	0.0258	(0.0019)	0.0989	(0.0031)
4	0	0.0136	(0.0024)	0.0428	(0.0012)
5	0	0.0070	—	0.0197	—
6	0	0.0183	(0.0013)	0.0671	(0.0015)
7	0	0.0085	(0.0033)	0.0300	(0.0036)

†95 min for Mixture 1

Table 16. Comparison of values of α obtained using results from different techniques.

Mixture	Technique					
	RPLC		DSC		FT-IR	
1	0.0667	(0.0024)	0.0389	(0.0143)	0.0868	(0.0221)
2	0.0219	(0.0005)	—	—	0.0375	(0.0122)
3	0.0989	(0.0031)	0.1013	(0.0094)	—	—
4	0.0428	(0.0012)	0.0275	(0.0120)	0.0327	(0.0232)
5	0.0197	—	—	—	—	—
6	0.0671	(0.0015)	0.0801	(0.0076)	—	—
7	0.0300	(0.0036)	0.0151	(0.0088)	0.0665	(0.0265)

The next stage in the analysis is to establish the relationship between the RPLC peak ratios and the parameters f, g, and α. We let the major epoxy (whose concentration is B) represent TGDDM, and the minor epoxy (concentration B') represent DGEBA. The concentrations of the respective one-to-one reaction products are C and C'. The LC peak area ratios will be proportional to the respective concentration ratios. Thus:

$$\frac{TGDDM}{DDS} \propto \frac{B}{A}, \qquad \frac{DGEBA}{DDS} \propto \frac{B'}{A}, \qquad \frac{RP}{DDS} \propto \frac{C}{A} \tag{12}$$

where the expressions on the left-hand side refer to the ratios of the areas of the LC peaks.

It was mentioned previously that the DGEBA peak is subject to interference from what appears to be a TGDDM-DDS reaction product. This must be taken into account in the analysis. This can be done by assuming that the contribution from the interfering component is proportional to the amount of the one-to-one TGDDM-DDS reaction product RP. Figure 13 shows a plot of the apparent DGEBA/DDS ratio versus the RP/DDS ratio for the two mixtures containing no DGEBA. The assumption is seen to be reasonable, and a constrained linear regression (forced through the origin) gives a slope of 0.197 with a standard error of 0.014. Thus the "true" DGEBA/DDS ratio is given by subtracting (0.197) (RP/DDS) from the measured ratio.

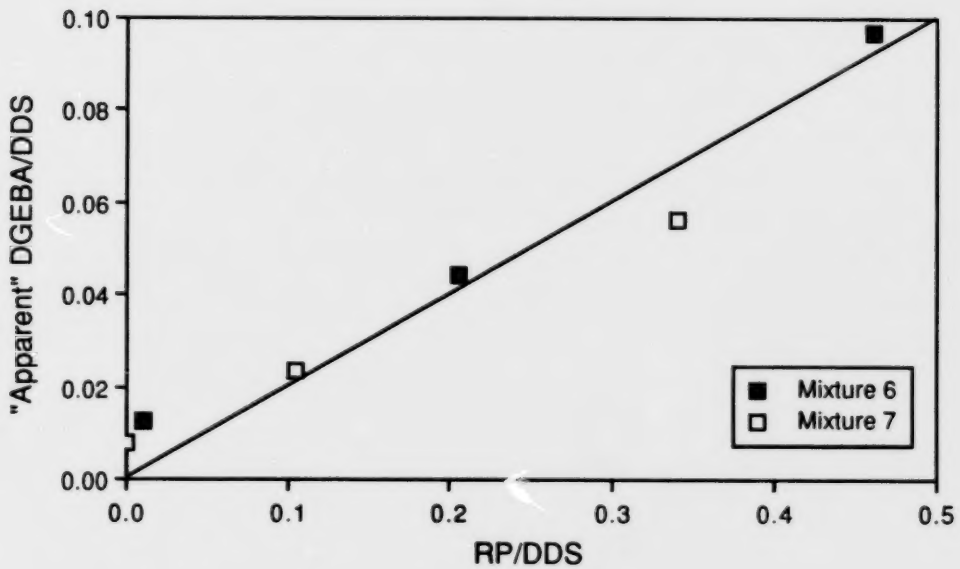


Figure 13. Variation of "apparent" DGEBA/DDS peak area ratio as a function of RP/DDS ratio.

Making use of Equations 6, 7, 8, 9, and 12, keeping only the first-degree terms, and introducing suitable proportionality constants, we obtain the following relationships:

$$\frac{TGDDM}{DDS} = K_1 f \left[1 + (f + g)\left(4 - \frac{1}{f + rg}\right)\alpha\right] \qquad (13)$$

$$\frac{DGEBA}{DDS} - (0.197)\left(\frac{RP}{DDS}\right) = K_2\, g\left[1 + (f + g)\left(4 - \frac{r}{f + rg}\right)\alpha\right] \qquad (14)$$

$$\frac{RP}{DDS} = K_3 f\left[\frac{f + g}{f + rg}\,\alpha\right] \qquad (15)$$

The constants K_1, K_2, K_3 take account of the different LC response factors for the different peaks. They also compensate to some extent for the fact that the epoxy resins used are not pure monofunctional compounds.

The next stage is to determine values for these constants as well as r, the ratio of the reactivity of the DGEBA resin relative to that of the TGDDM resin. There are thus 4 unknown quantitites to determine based on 21 known quantities (3 ratios for each of 7 mixtures). This means that the problem is considerably over-determined, so that the validity of the model can be easily verified.

To determine K_1, we make use of Equation 13 together with the data for the unheated mixtures. In this case, $\alpha = 0$ and Equation 13 reduces to:

$$\frac{TGDDM}{DDS} = K_1 f \qquad (16)$$

Figure 14 shows a plot of TGDDM/DDS versus f for the seven unheated mixtures. An excellent linear correlation is observed, and constrained linear regression gives a slope of 1.682 with a standard error of 0.015. Thus $K_1 = 1.682$.

K_2 is determined using a similar procedure. Since both α and RP are equal to zero for the unheated mixtures, Equation 14 becomes:

$$\frac{DGEBA}{DDS} = K_2\, g \qquad (17)$$

Again, a plot (Figure 15) gives a good straight line, with a slope of 1.517 and a standard error of 0.026. Thus $K_2 = 1.517$.

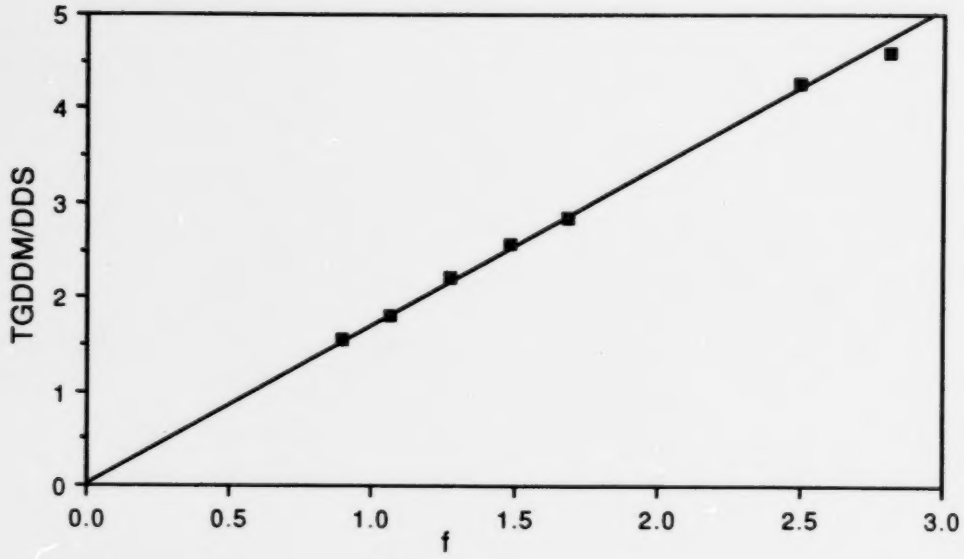


Figure 14. Variation of TGDDM/DDS peak area ratio as a function of f for the seven unheated mixtures.

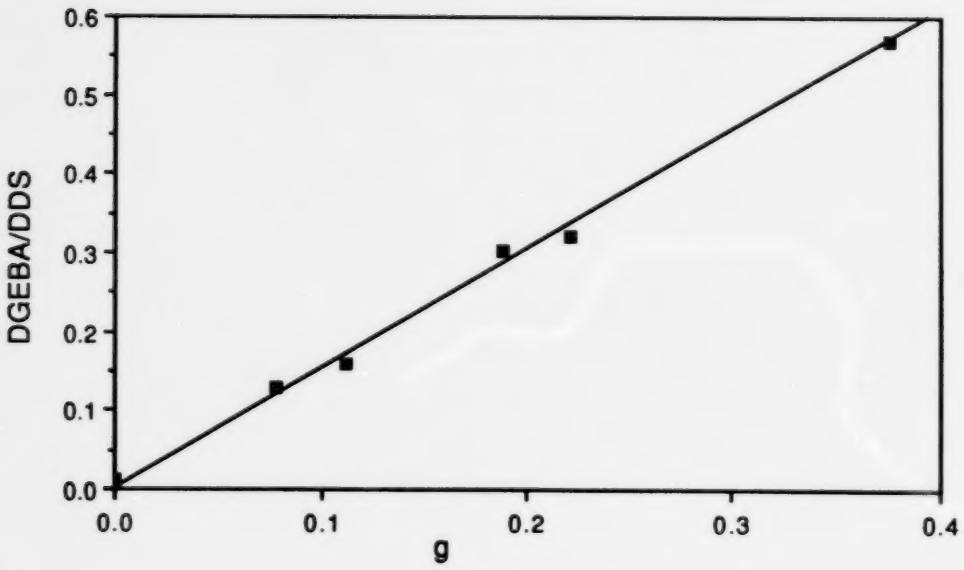


Figure 15. Variation of DGEBA/DDS peak area ratio as a function of g for the seven unheated mixtures.

Rearrangement of Equation 15 gives the following equation:

$$\frac{1}{f}\frac{RP}{DDS} = K_3\left[\frac{f+g}{f+rg}\alpha\right] \tag{18}$$

which for the special cases g = 0 or r = 1, reduces to:

$$\frac{1}{f}\frac{RP}{DDS} = K_3\alpha \tag{19}$$

In Figure 16, the quantity on the left is plotted against α (from Table 15) for all seven mixtures studied. Generally speaking, the approximation of linear behaviour with respect to α is seen to be good. Constrained linear regression was used to calculate the slope for each mixture, and the results are given in Table 17.

Table 17. Results of calculations based on Figure 16.

Mixture	Slope	Std. Error	Calcd. r
1	5.738	0.278	2.22
2	5.683	0.104	2.46
3	5.289	0.259	4.51
4	5.632	0.042	3.89
5	5.279	0.079	5.51
6	6.768	0.747	—
7	6.773	0.109	—

It is encouraging to see that mixtures #6 and #7, for which g = 0, give practically the same slope, as expected from Equation 19. Based on the average of the two, we set K_3 equal to 6.770. If r were equal to 1, the other mixtures should give the same slope. The fact that they are somewhat lower suggests that r is greater than 1. By applying Equation 18, we can calculate a value of r for each mixture from the slope and the value just derived for K_3. The results are given in the last column of Table 17. It is seen that the value of r is not well-determined, although it is obvious that it is greater than 1, that is, that the DGEBA is more reactive than the TGDDM. The average of the five values in Table 17 is 3.72, which we take as the value for r. It is close to the value obtained for Mixture #4, which is believed to be the one closest to Narmco 5208 in composition.

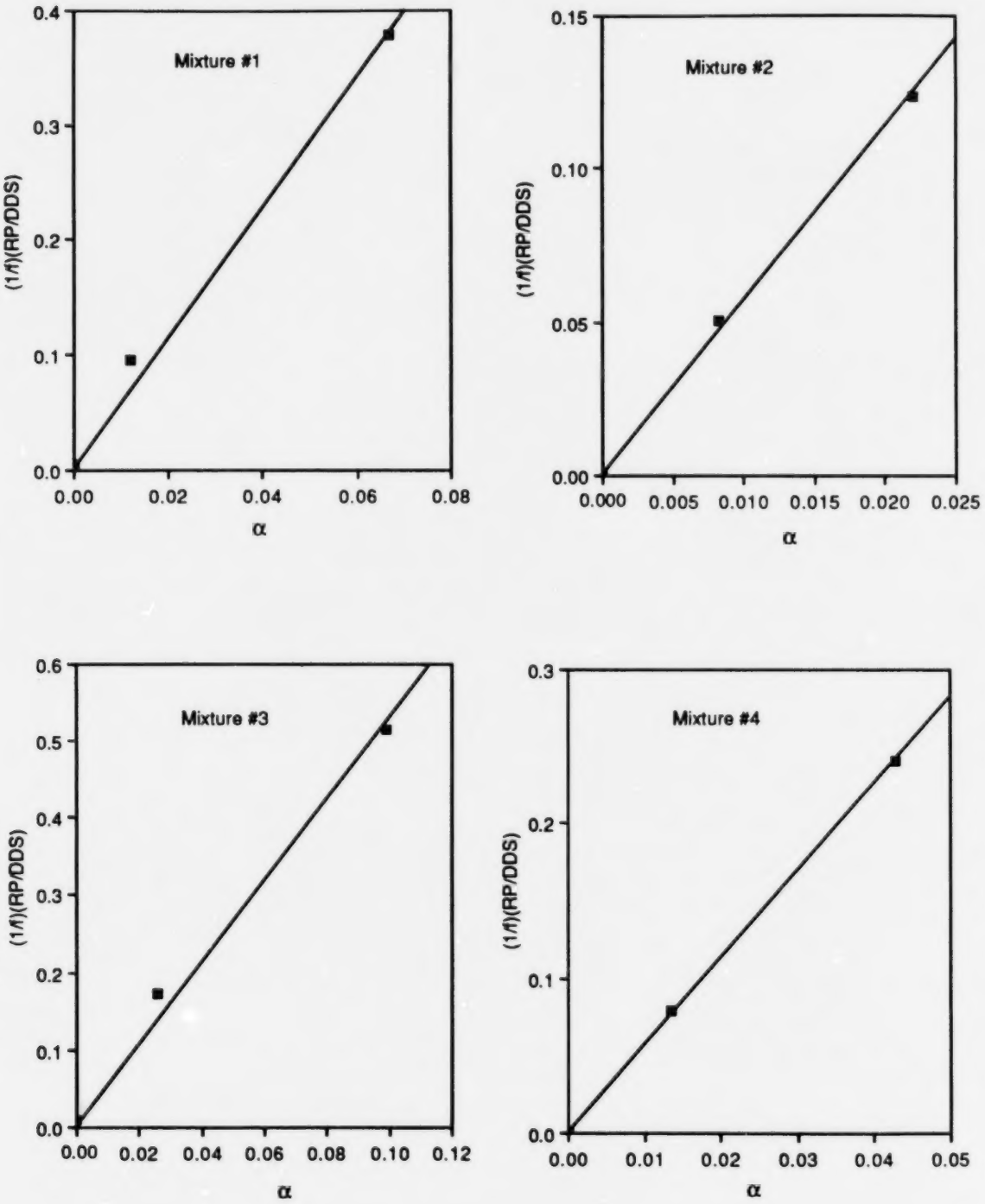


Fig. 16(a). Relationship between (1/f)(RP/DDS) and α for mixtures #1 to #4.

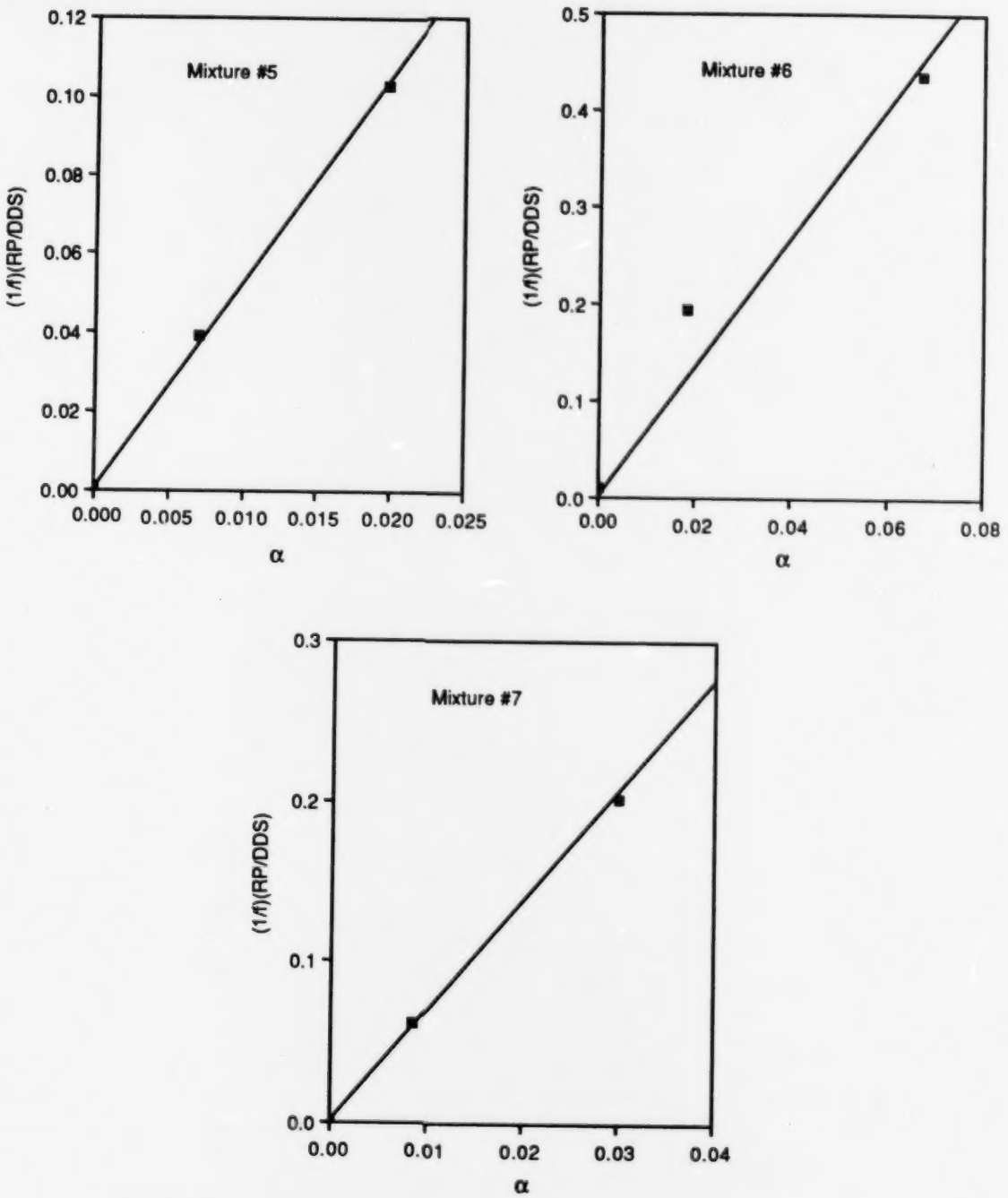


Fig. 16(b). Relationship between (1/f)(RP/DDS) and α for mixtures #5 to #7.

The variation of TGDDM/DDS and DGEBA/DDS with α has not been used in the analysis so far. Using Equations 13 to 15, together with the values derived for K_1, K_2, K_3, and r, we can calculate this variation and compare it to the experimental results. This will serve as a check on the validity of the assumed model. Figures 17 and 18 show that the calculated variation, represented by the solid lines, is in good agreement with the experimental data, represented by the points.

This completes the model, and it is now possible to calculate f, g, and α from the RPLC results using Equations 13, 14, and 15. To simplify the calculation, we define the following quantities:

$$Q_1 = \frac{1}{K_1}\frac{TGDDM}{DDS} = f\left[1 + (f + g)\left(4 - \frac{1}{f + rg}\right)\alpha\right] \tag{20}$$

$$Q_2 = \frac{1}{K_2}\left[\frac{DGEBA}{DDS} - (0.197)\left(\frac{RP}{DDS}\right)\right] = g\left[1 + (f + g)\left(4 - \frac{r}{f + rg}\right)\alpha\right] \tag{21}$$

$$Q_3 = \frac{1}{K_3}\frac{RP}{DDS} = f\left[\frac{f + g}{f + rg}\,\alpha\right] \tag{22}$$

where $K_1 = 1.682$, $K_2 = 1.517$, $K_3 = 6.770$, and $r = 3.72$. By inverting these equations we obtain:

$$P = \frac{g}{f} = \frac{Q_2}{Q_1 + (1 - r)Q_3} \tag{23}$$

$$f = \frac{Q_1 + Q_3}{1 + 4Q_3(1 - rP)} \tag{24}$$

$$g = fP \tag{25}$$

$$\alpha = \frac{Q_3}{f}\frac{1 + rP}{1 + P} \tag{26}$$

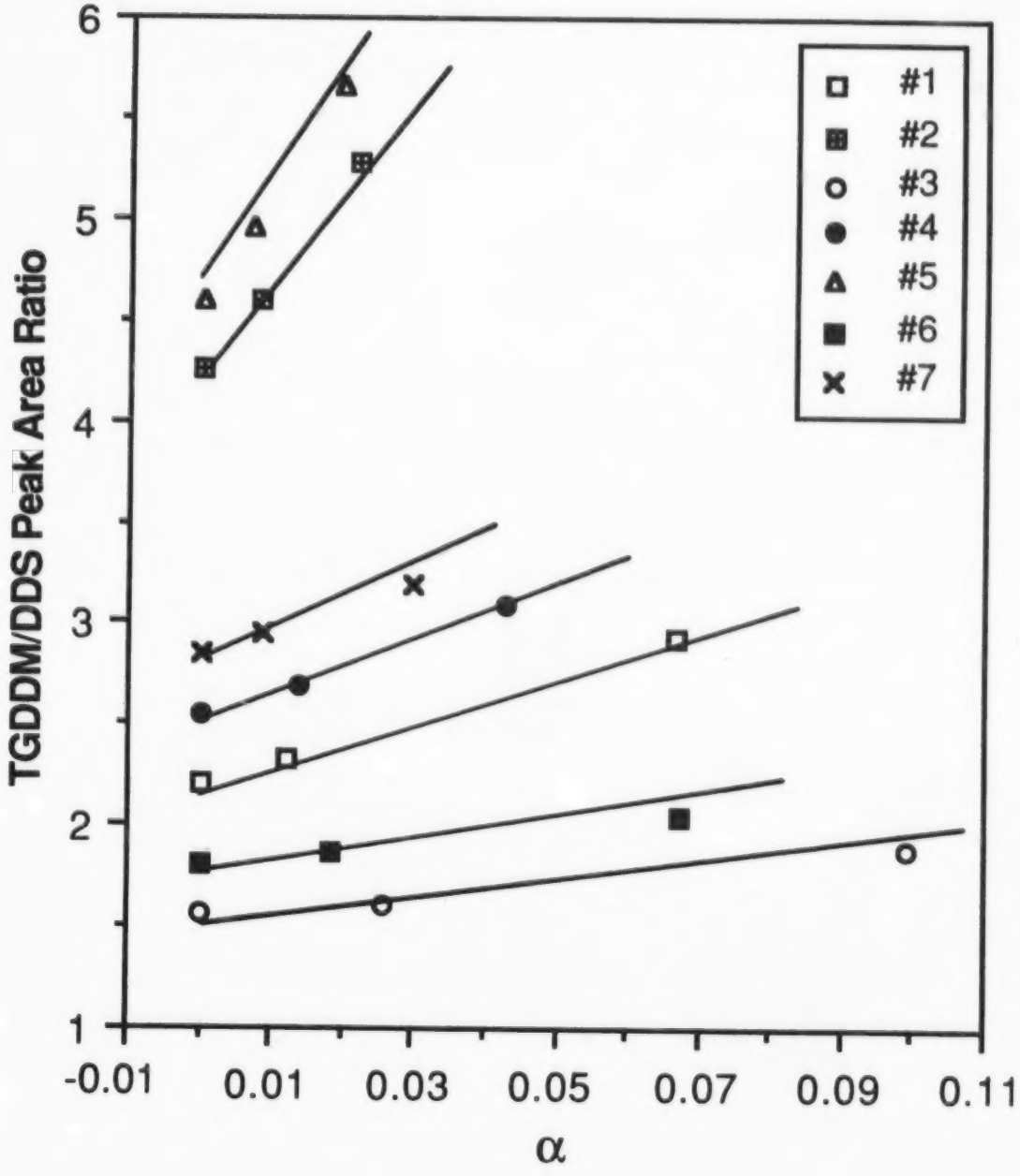


Fig. 17. Relationship between the TGDDM/DDS peak area ratio and α. Comparison of experimental values (symbols) and values predicted by the model (solid lines).

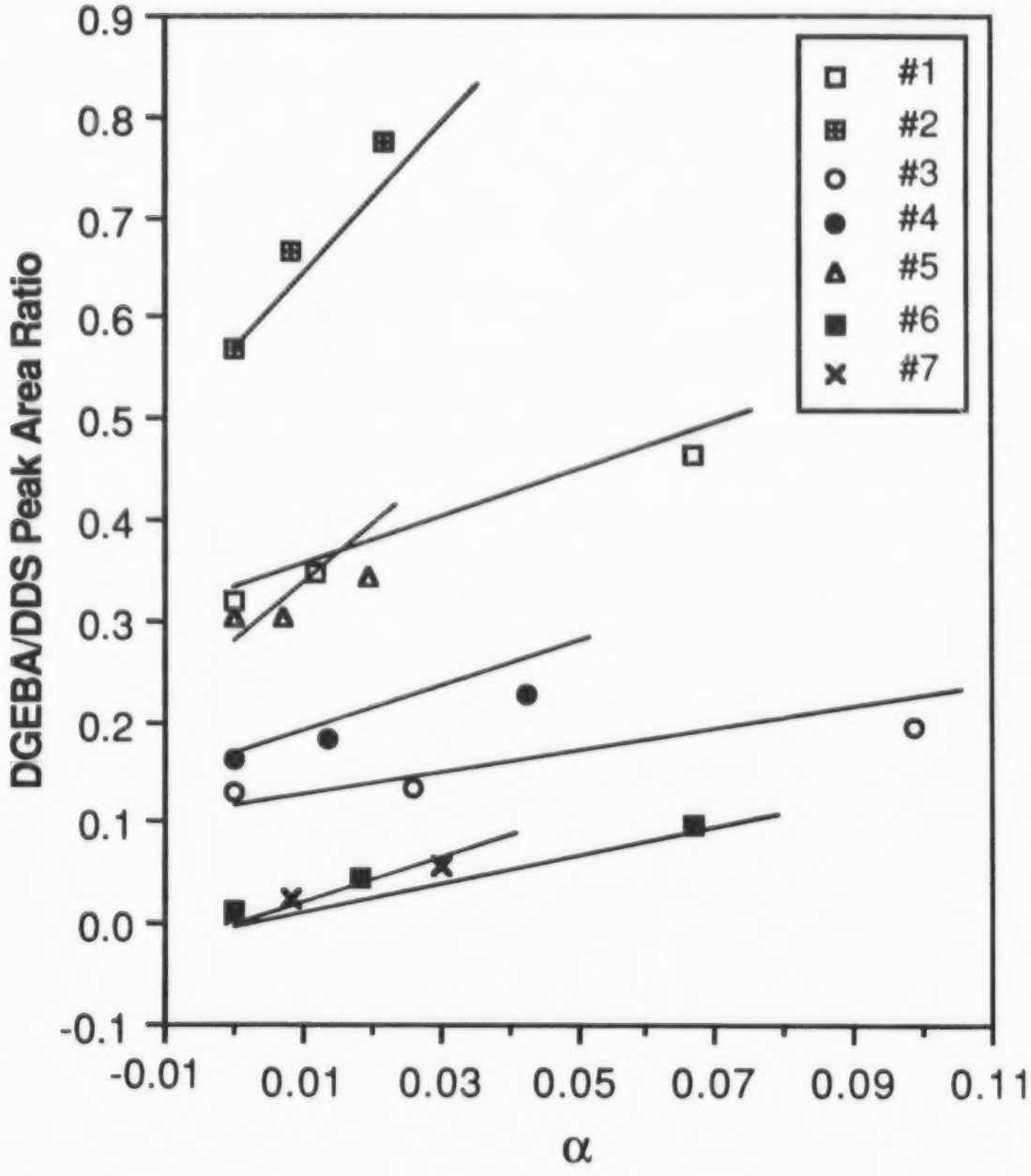


Fig. 18. Relationship between the DGEBA/DDS peak area ratio and α. Comparison of experimental values (symbols) and values predicted by the model (solid lines).

Once f and g are known it is possible to calculate the percentages of the original three components using Equations 1 and 2:

$$\%\,HT\,976 \;=\; 100 \times \left[\frac{\frac{1}{1.611}}{\frac{1}{1.611} + \frac{f}{0.768} + \frac{g}{0.440}} \right] \tag{27}$$

$$\%\,MY\,720 \;=\; 100 \times \left[\frac{\frac{f}{0.768}}{\frac{1}{1.611} + \frac{f}{0.768} + \frac{g}{0.440}} \right] \tag{28}$$

$$\%\,SU\,8 \;=\; 100 \times \left[\frac{\frac{g}{0.440}}{\frac{1}{1.611} + \frac{f}{0.768} + \frac{g}{0.440}} \right] \tag{29}$$

Thus, by using Equations 20 to 29 it is possible, starting with the three peak area ratios obtained from the RPLC chromatogram, to calculate the percentages of the three components present in a sample of Narmco 5208, as well as the degree of polymerization α. In Table 18 are shown the results of such calculations for the seven mixtures involved in the above analysis, as well the extra mixture #5a. Since the latter was not used in the calibration procedure, it serves as a validation sample. For each mixture there are three sets of data corresponding to the three stages of heating. The RPLC peak area ratios used for the calculation are taken from Tables 12 to 14. The Δ values correspond to the differences between the calculated and the "true" values, which are taken from Tables 2 (composition) and 15 (α). It is seen that, with very few exceptions, the calculated amounts of the different starting components agree with the true values within 1 weight percent. The standard deviations, based on the 21 "calibration" samples, are 0.57 wt % for the HT976, 0.74 wt % for the MY720, and 0.87 wt % for the SU-8. Thus the DDS content appears to be determined with somewhat better accuracy than the epoxy contents.

Table 20 gives results calculated for several samples of Narmco 5208 prepreg and resin, based on the RPLC data given in Table 19. Since the true composition of these commercial samples is unknown, it is impossible to check the accuracy of the results. However, it is interesting to compare the results for the different batches. All were typical lots of prepreg based on woven carbon fibres, except Batch 1047, which consisted of neat resin coated on a plastic sheet, and Batch 1023, which consisted of neat resin in bulk form. In the case of Batch 1022, two different rolls were tested: Roll Number 6, which had

never been opened previously, and Roll Number 3, which had already been opened for use.

Table 18. Composition and degree of polymerization α for the prepared mixtures, as calculated from the RPLC peak area ratios according to the proposed model. The three sets of results for each mixture correspond to the three stages of polymerization: unheated, heated at 120°C for 30 min ('), and heated for 80 min (").

Mixture	%HT976		%MY720		%SU-8		α	
	Calc.	Δ	Calc.	Δ	Calc.	Δ	Calc.	Δ
#1	22.22	-0.05	60.70	0.97	17.08	-0.92	0.0011	0.0011
#1'	22.84	0.57	60.26	0.53	16.90	-1.10	0.0196	0.0076
#1"	23.09	0.82	60.39	0.66	16.52	-1.48	0.0784	0.0117
#2	13.00	-0.13	69.11	0.31	17.89	-0.19	0.0000	0.0000
#2'	13.19	0.06	68.04	-0.76	18.78	0.70	0.0103	0.0021
#2"	13.18	0.05	68.22	-0.58	18.60	0.52	0.0253	0.0033
#3	30.91	-0.63	59.64	0.15	9.44	0.47	0.0018	0.0018
#3'	32.62	1.08	59.51	0.02	7.87	-1.10	0.0312	0.0054
#3"	32.46	0.92	59.84	0.35	7.69	-1.28	0.0922	-0.0067
#4	21.90	-0.15	69.66	0.74	8.44	-0.59	0.0002	0.0002
#4'	22.33	0.28	69.42	0.50	8.25	-0.78	0.0138	0.0002
#4"	22.38	0.33	70.23	1.31	7.39	-1.64	0.0409	-0.0020
#5	13.37	0.20	76.80	-0.98	9.82	0.77	0.0000	0.0000
#5'	13.51	0.34	77.76	-0.02	8.73	-0.32	0.0069	-0.0001
#5"	13.33	0.16	78.71	0.93	7.96	-1.09	0.0175	-0.0022
#6	30.58	-0.43	68.64	-0.35	0.78	0.78	0.0015	0.0015
#6'	31.85	0.84	67.87	-1.12	0.29	0.29	0.0301	0.0118
#6"	32.10	1.09	67.47	-1.52	0.43	0.43	0.0687	0.0016
#7	21.89	-0.14	77.71	-0.26	0.41	0.41	0.0000	0.0000
#7'	22.27	0.24	77.58	-0.39	0.15	0.15	0.0093	0.0009
#7"	22.77	0.74	77.80	-0.17	-0.57	-0.57	0.0305	0.0005
#5a	13.77	0.32	77.49	0.26	8.73	-0.59		
#5a'	13.86	0.41	77.17	-0.06	8.96	-0.36		
#5a"	13.79	0.34	77.46	0.23	8.75	-0.57		

Table 19. RPLC results (based on peak areas) for different batches of Narmco 5208.

Batch	DDS Peak	TGDDM Peak	DGEBA Peak	RP Peak	TGDDM / DDS	DGEBA / DDS	RP / DDS
1022-3	4.280	13.46	1.594	1.470	3.145	0.372	0.344
1022-6	4.361	13.52	1.570	1.327	3.101	0.360	0.304
1103	4.810	13.56	1.879	1.204	2.819	0.391	0.250
1101	3.600	12.72	1.324	1.742	3.533	0.368	0.484
1104	4.311	13.19	1.626	1.336	3.060	0.377	0.310
1010	3.719	12.70	1.185	1.785	3.415	0.319	0.480
1014	4.130	13.37	1.552	1.623	3.237	0.376	0.393
1047	4.795	13.54	0.792	1.110	2.824	0.165	0.232
1023	3.034	12.33	0.709	2.406	4.064	0.234	0.793

Table 20. Composition and degree of polymerization α for different batches of Narmco 5208, as calculated from the RPLC peak area ratios of Table 19 according to the proposed model.

Batch	f	g	f+g	α	HT976 (wt %)	MY720 (wt %)	SU-8 (wt %)
1022-3[a]	1.488	0.173	1.661	0.0437	21.0	65.7	13.3
1022-6[a]	1.503	0.173	1.676	0.0383	20.9	65.9	13.2
1103[b]	1.397	0.199	1.596	0.0355	21.5	62.9	15.7
1101[b]	1.567	0.148	1.715	0.0563	20.7	68.1	11.2
1104[b]	1.472	0.181	1.653	0.0403	21.1	65.0	14.0
1010[b]	1.536	0.123	1.659	0.0555	21.4	68.9	9.7
1014[b]	1.493	0.166	1.659	0.0495	21.1	66.1	12.8
1047[c]	1.474	0.073	1.548	0.0262	22.9	70.9	6.2
1023[d]	1.677	0.041	1.718	0.0743	21.4	75.4	3.2

[a]Prepreg — suffixes indicate different rolls of same batch.
[b]Prepreg.
[c]Neat resin coated on plastic sheet.
[d]Neat resin in bulk form.

We first consider only the prepreg samples. The most remarkable observation to be made is the consistency of the calculated HT976 content, which lies in the range of 21.1 ± 0.4 %. This quantity appears to be well determined by the method. The calculated epoxy contents show somewhat more variation, being 66.1 ± 3.2 % for MY720 and 12.8 ± 3.2 % for the SU-8. It is not clear whether these variations are real or not, since there are several factors which make the determination of the epoxy content more difficult than that of the hardener. The model described in the Appendix assumes the epoxies to be pure monofunctional monomers. However, unlike the hardener, the real epoxies are complex mixtures of various different molecules, only one of which is monitored by RPLC. In the case of MY720, it is the monomer TGDDM, which accounts for about 68% by weight of the MY720. However, for SU-8, it is DGEBA, which corresponds to only about 10% of the total weight. The accuracy of the method depends on the consistency of the starting materials MY720 and SU-8, i.e. on the assumption that the batches of MY720 and SU-8 used to make the different lots of prepreg have the same composition as the samples used for the calibration. This may be the principal cause of the variations observed, since any variation in the DGEBA content of the SU-8 would be reflected in the apparent SU-8 content of the prepreg. A second factor which must be considered is the manufacturing procedure for the prepreg. The calibration mixtures were prepared by mixing the three components together and heating at 120°C; thus both epoxies react with the DDS for the same time. It is possible that in the prepreg manufacture a different mixing procedure is used, or that the processing temperature is considerably different from 120°C, and this would obviously influence the results. Yet another source of uncertainty is the interference observed between the DGEBA peak and the peak of the unknown reaction product. Although a correction was applied, some error may result. Because of these complications, the individual epoxy contents are subject to some uncertainty. However, the hardener content, and hence the total epoxy content and the epoxy-to-hardener ratio, appears to be determined with good precision.

The degree of polymerization α is also believed to be determined with reasonable precision, since it is based on the intensity of the well-defined reaction product peak. For the prepreg samples, it varies between 0.036 and 0.056, and the differences are believed to be significant. It is not clear whether they existed at the time of manufacture or whether they are the result of subsequent aging. It is interesting to compare the results for the two rolls of Batch 1022. Both give the same composition, as expected, but Roll #3 gives a higher value of α than Roll #6. This is because Roll #6 had not been previously thawed, whereas Roll #3 had been opened for use at some point.

Based on the above results, a typical batch of Narmco 5208 prepreg is seen to have the following properties: HT976 content 21% by weight, MY720 content 66%, SU-8 content 13%, degree of polymerization $\alpha = 0.04$. Comparison with Table 1 shows general agreement, except that the SU-8 content is somewhat higher. In spite of the difficulties

mentioned above, the analysis reported here is believed to be more accurate because it takes into account the partial polymerization of the system. Carpenter, for instance, determined the SU-8 content from the DGEBA peak but neglected the partial reaction [8]. Since we have shown that the DGEBA reacts faster than the TGDDM, this is not insignificant. For example, if we consider the RPLC results for Mixture #4, on going from the unheated mixture to the one heated for 80 min ($\alpha = 0.043$), the TGDDM normalized peak area drops by 9%, whereas the corrected DGEBA peak area drops by 27%! Assuming that a similar decrease occurs in typical prepreg, if the original SU-8 content were 13%, the apparent content in the prepreg would then be only 9.5%, which is the same as the result reported by Carpenter (9.4%). The other results given in Table 1 were obtained using various techniques. The total hardener content was generally determined by FT-IR; the average result is 21.5%, which is in excellent agreement with the result obtained here.

We now consider the two special batches. Batch 1047 has a significantly lower degree of advancement than the prepreg batches. The hardener content appears slightly higher, and the SU-8 content definitely lower. Batch 1023 also appears to have a low SU-8 content, but is highly advanced. It is believed that this sample was heated in order to transfer it to the container in which it was received, and this caused further polymerization. It is not known whether the low apparent SU-8 content is real or the result of a different manufacturing procedure.

In previous work [13] Batch 1014 was used for an in-depth study of the effects of aging on the prepreg. Samples were exposed at room temperature and 50% relative humidity and analyzed at intervals up to 66 days. The RPLC data obtained were used to calculate the composition and degree of polymerization using the method derived in this work. The results are given in Table 21, together with those for the FT-IR epoxide index. Up to about 29 days aging, the behaviour is as expected. The calculated composition remains reasonably consistent, while α increases steadily. Beyond this point, however, deviations occur and the method does not work well. Figures 20 and 21 show graphically the behaviour observed for the HT976 content and α. Over the first 29 days, the calculated HT976 content has an average value of 20.6% with a standard deviation of 0.3% (absolute). After this, it begins to decline. Similarly, over the first 29 days the calculated α increases linearly with time, but beyond this point it tends to level off. The reason for this is that after 29 days, the resin has advanced to the point where the first-order approximation used in developing the model is no longer valid, that is, the linear relationship between the measured quantities and α no longer applies. As shown in Figure A-3 of the Appendix, the single-epoxy model predicts that when α reaches about 0.15 the amount of initial reaction product begins to drop because of further reaction. Deviation from linearity occurs before this point. The RPLC results given in Ref. 13 confirm that similar behaviour occurs in the Narmco 5208 system. The RP peak shows a maximum

around 30 days aging time and begins to decrease after this. Thus the proposed method appears to be valid up to about 30 days aging, at which point α is equal to 0.08, or double the typical value for prepreg when it is received.

Figure 22 shows the relationship between the FT-IR epoxide index and α. For the samples aged less than 30 days, there is a reasonably good linear relationship.

Table 21. Results obtained on applying the method derived in this work to the data from the previous aging study [13].

Aging Time (days)	FT-IR Epoxide Index	Results calculated using present method			
		α	% HT976	% MY720	% SU-8
0	0.409	0.046	20.8	65.3	13.9
2	0.405	0.048	21.3	65.7	12.9
4	0.400	0.051	20.7	66.7	12.6
7	0.397	0.052	20.4	66.7	12.9
9	0.391	0.054	20.8	66.5	12.7
11	0.393	0.056	20.7	66.8	12.5
14	0.387	0.061	20.9	66.6	12.5
17	0.388	0.060	20.3	68.0	11.7
21	0.376	0.069	20.7	67.8	11.6
25	0.376	0.073	20.4	68.5	11.1
29	0.365	0.077	20.3	69.0	10.7
32	0.359	0.077	20.0	70.2	9.9
35	0.355	0.078	19.2	70.3	10.5
38	0.357	0.079	19.3	71.3	9.4
42	0.354	0.082	18.3	73.2	8.6
45	0.345	0.081	17.9	73.6	8.5
52		0.083	17.4	75.1	7.5
59		0.086	16.6	76.2	7.2
66		0.096	16.0	78.9	5.2

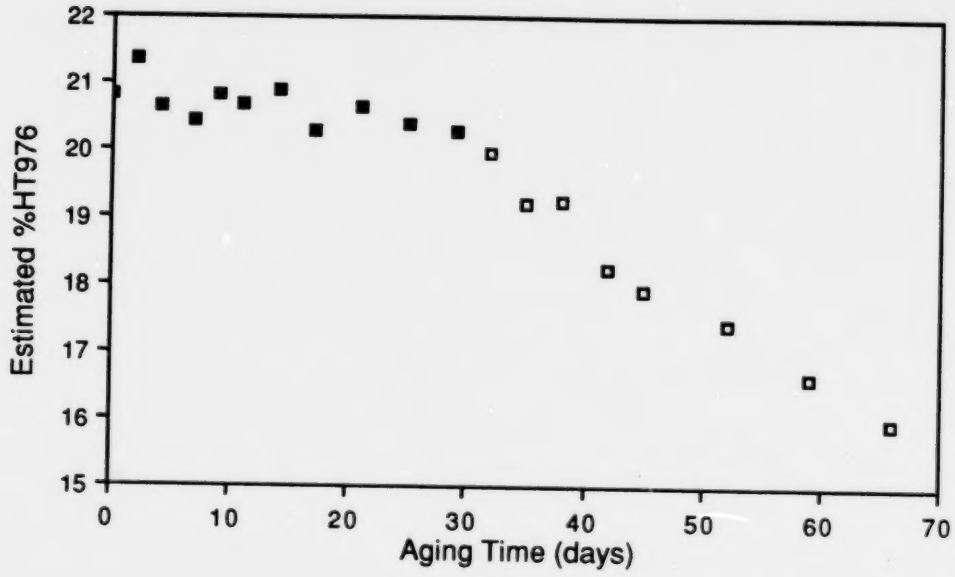


Figure 20. Variation of calculated HT976 content with extent of aging for prepreg samples aged at room temperature and 50% relative humidity. Unfilled symbols correspond to aging times longer than 30 days.

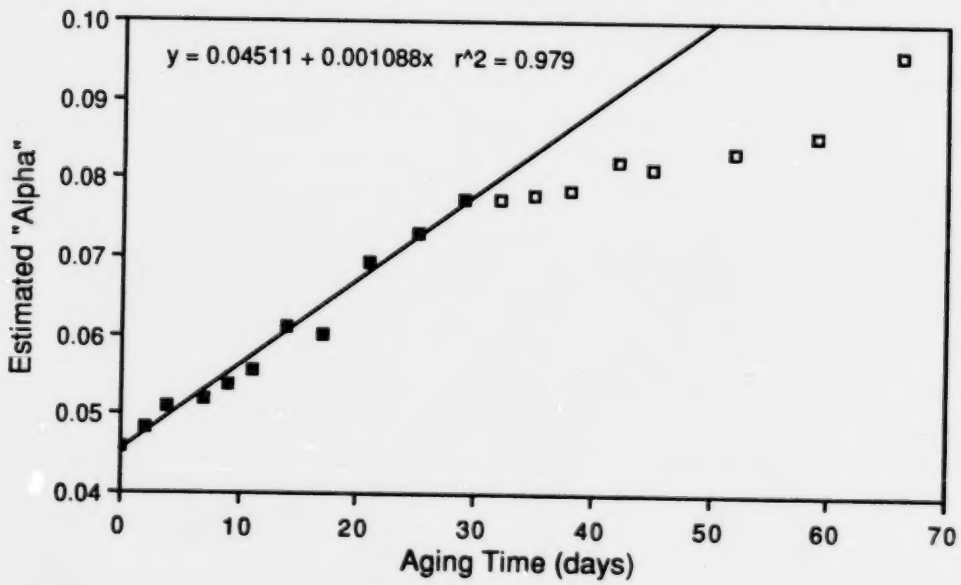


Figure 21. Variation of calculated degree of polymerization α with extent of aging for prepreg samples aged at room temperature and 50% relative humidity. Unfilled symbols correspond to aging times longer than 30 days.

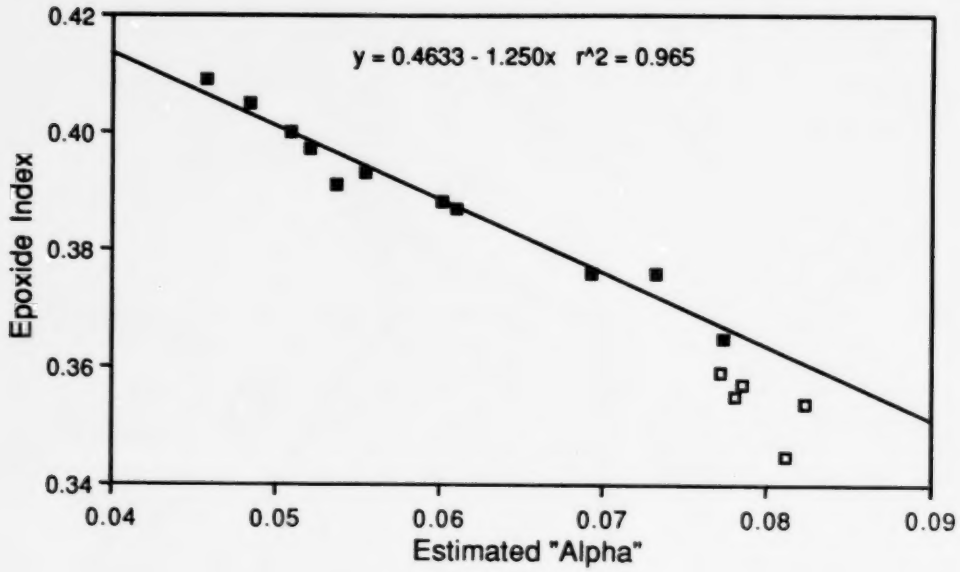


Figure 22. Relationship between FT-IR epoxide index and degree of polymerization α for prepreg samples aged at room temperature and 50% relative humidity. Unfilled symbols correspond to aging times longer than 30 days.

For some of the prepreg samples analyzed, the heat of polymerization ΔH had been determined by differential scanning calorimetry followed by thermogravimetric analysis, according to a method previously developed [11]. From the data generated in this work, it is possible to calculate values for ΔH which may then be compared to the experimental ones. This is done by taking the composition determined by RPLC, calculating the number of moles of epoxy per gram initially present using the equivalent weights given on page 6, correcting for the partial polymerization α, and multiplying by the figure of 106.2 kJ/mol obtained for the calibration mixtures. The results are:

Prepreg Sample	ΔH (Estimated)	ΔH (Experimental) & S.D.
1022-3	571.6	572.7 (1.8)
1022-6	576.3	588.4 (10.6)
1014 (0 days aging)	570.1	548.3 (3.5)

The good agreement observed offers further support for the validity of the method.

3.5 HIGH-PERFORMANCE SIZE-EXCLUSION CHROMATOGRAPHY (HPSEC)

The prepared mixtures were also analyzed by high-performance size-exclusion chromatography using the method described in an earlier report [11]. A "degree of polymerization index" is calculated by dividing the areas of the peaks corresponding to high-molecular-weight components by the area of the peaks corresponding to the monomers. In Figure 19, the DP Index is plotted against α for the seven mixtures studied. In most cases a very good linear relationship is observed, but the coefficients of the lines describing them vary depending on the composition of the particular mixture, so a general relationship cannot be derived. However, the results indicate that with suitable calibration using the typical composition, the DP Index could serve as a good quantitative indicator of the degree of polymerization.

4. CONCLUSION

The best method for characterizing a given batch of Narmco 5208 prepreg for kinetic modelling purposes appears to be reverse-phase liquid chromatography. Using methods developed previously [11], the three peak area ratios TGDDM/DDS, DGEBA/DDS, and RP/DDS are determined. Then by means of the model developed in this work (Eqs. 20 to 29), these data are used to estimate the percentage of each component present as well as the initial degree of polymerization α. The latter is determined with good accuracy, as is the hardener content. The individual contents of the two epoxy resins are determined somewhat less precisely because of complications related to the minor epoxy. The typical composition of Narmco 5208 prepreg is: 21% HT976, 66% MY720, 13% SU-8, and α = 0.04. The method gives good results for samples with α less than 0.08. For more advanced resin, the linear approximation used in the model is no longer valid.

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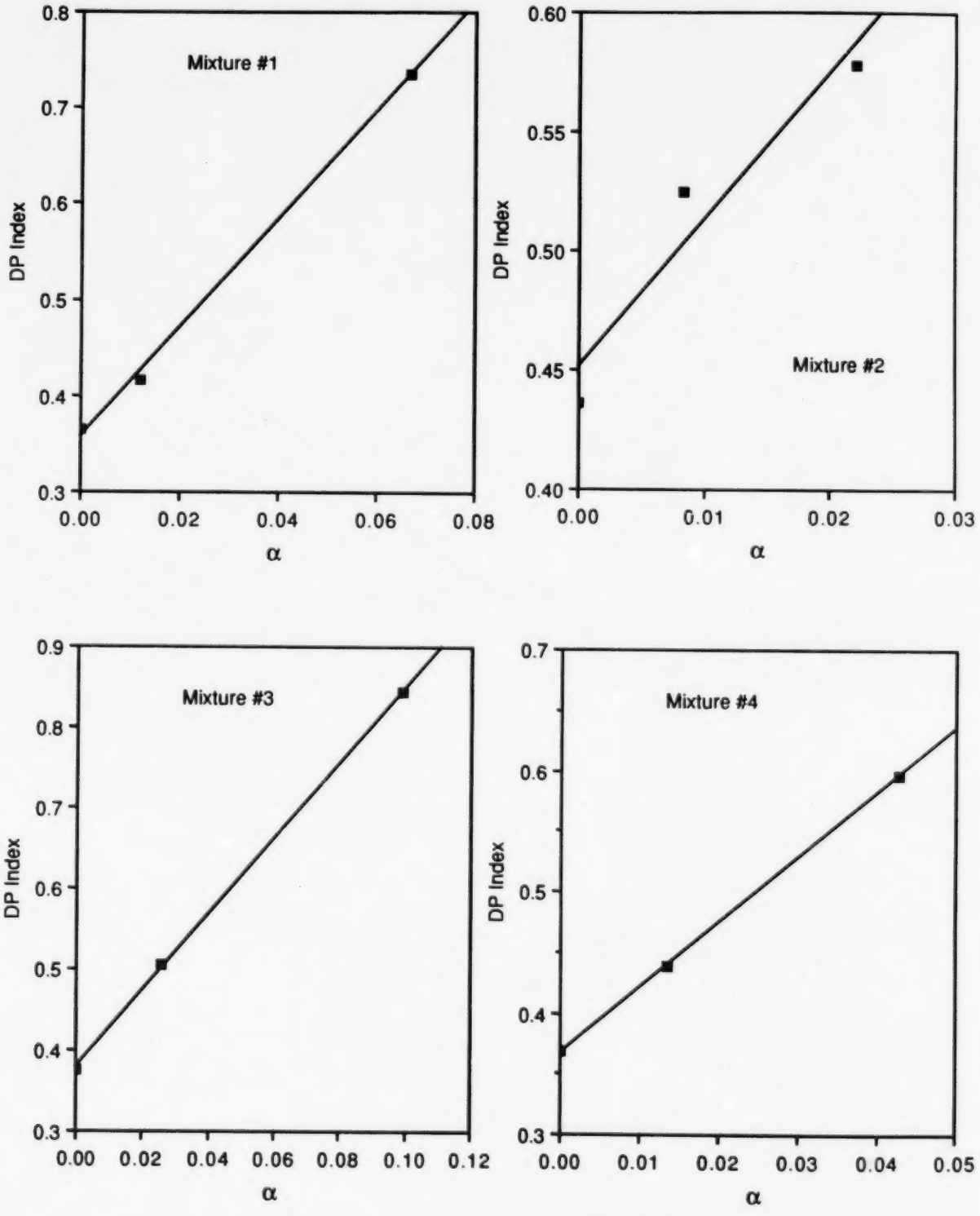

Fig. 19(a). Relationship between the "degree of polymerization index", as measured by HPSEC, and α for mixtures #1 to #4.

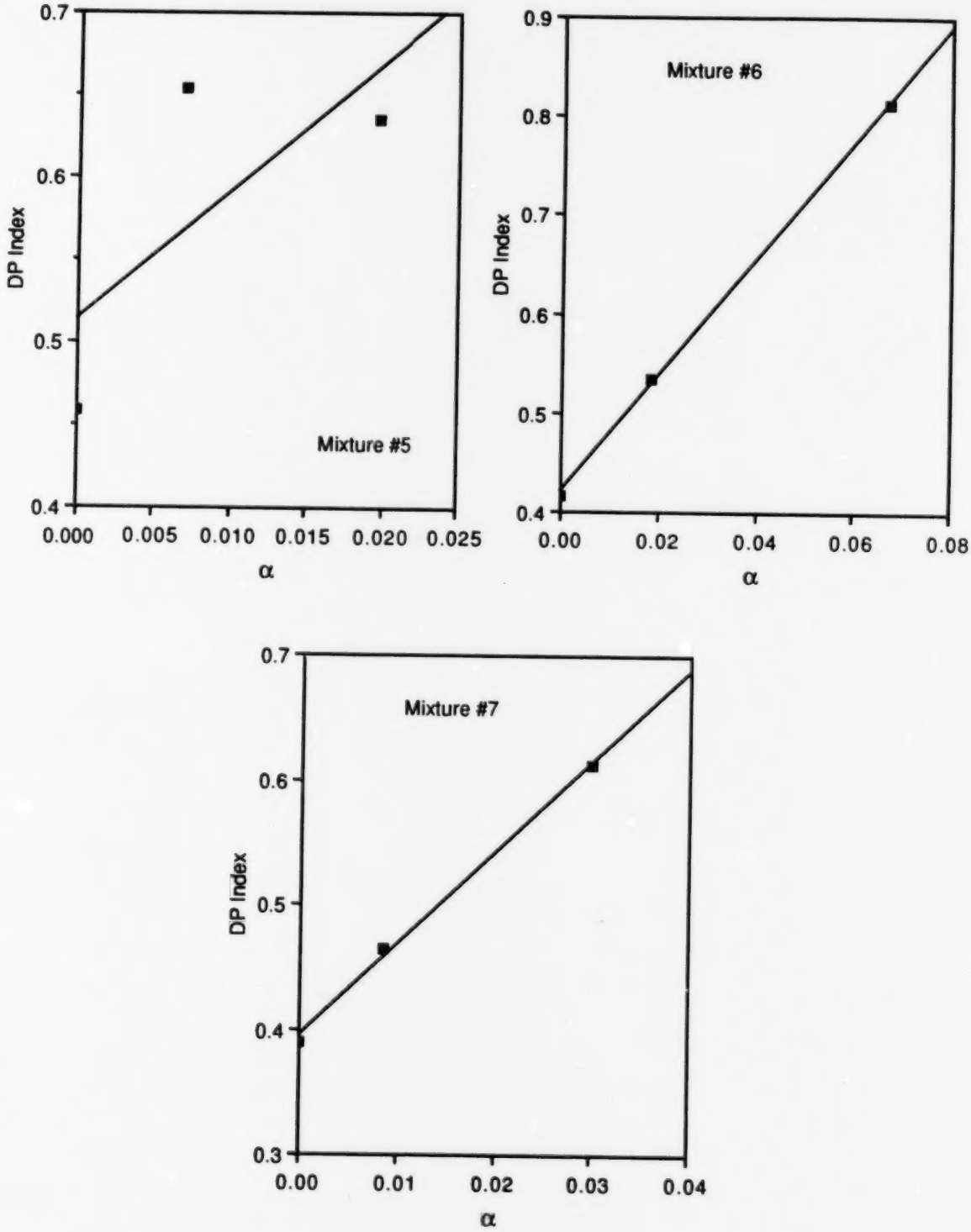

Fig. 19(b). Relationship between the "degree of polymerization index", as measured by HPSEC, and α for mixtures #5 to #7.

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APPENDIX A

SINGLE-EPOXY MODEL:

We consider first a simple model in which DDS reacts with a single monofunctional epoxy. The chemical formulae of the various molecules involved are given in Figure A-1. They are designated by the letters **A** to **G** as shown. We define the following parameters:

$A, B, \ldots G$ = Concentrations of the different components **A** to **G** at a given time t.

A_0, B_0 = Concentrations of the two starting components at $t = 0$

$f = B_0/4A_0$ = Epoxide-to-amine ratio (= 1 for a stoichiometric mixture in which each amine group reacts with two epoxide rings).

k_1 = Rate constant for the reaction between a primary amine group and an epoxide ring.

k_2 = Rate constant for the reaction between a secondary amine group and an epoxide ring.

The reaction scheme is as follows:

$$\mathbf{A} + \mathbf{B} \xrightarrow{2k_1} \mathbf{C}$$

$$\mathbf{B} + \mathbf{C} \xrightarrow{k_1} \mathbf{D}$$

$$\mathbf{B} + \mathbf{C} \xrightarrow{k_2} \mathbf{E}$$

$$\mathbf{B} + \mathbf{D} \xrightarrow{2k_2} \mathbf{F}$$

$$\mathbf{B} + \mathbf{E} \xrightarrow{k_1} \mathbf{F}$$

$$\mathbf{B} + \mathbf{F} \xrightarrow{k_2} \mathbf{G}$$

The coefficient 2 appears in some cases when there are two equivalent groups in the same molecule, so the probability of reaction is assumed to be doubled.

The following are the kinetic equations for the above reaction scheme:

$$\frac{dA}{dt} = -2k_1AB \tag{1}$$

$$\frac{dB}{dt} = -2k_1AB - k_1BC - k_2BC - 2k_2BD - k_1BE - k_2BF \tag{2}$$

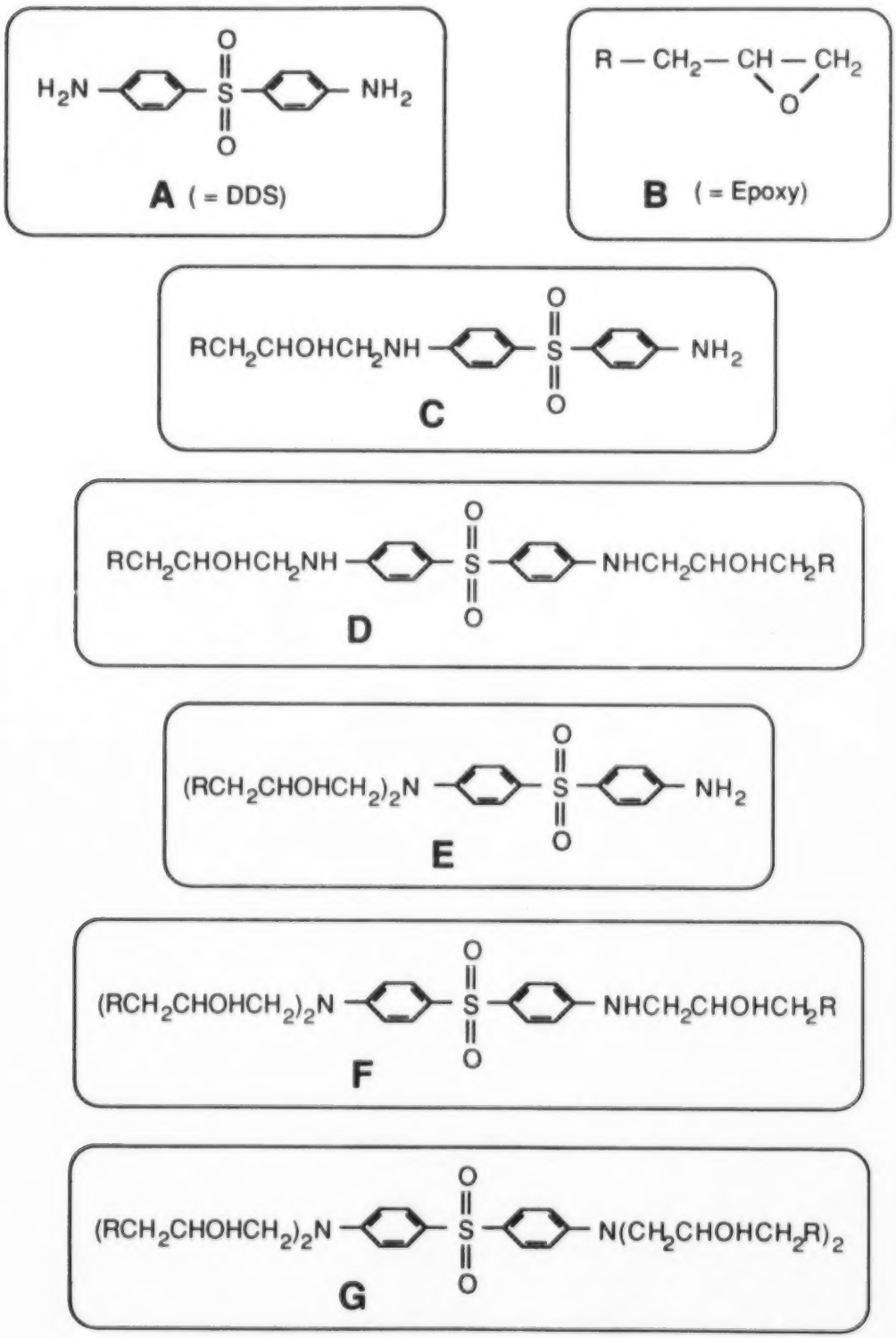

Fig. A-1. Chemical structures of molecules involved in DDS-epoxy reaction scheme.

$$\frac{dC}{dt} = +2k_1AB - k_1BC - k_2BC \tag{3}$$

$$\frac{dD}{dt} = +k_1BC - 2k_2BD \tag{4}$$

$$\frac{dE}{dt} = +k_2BC - k_1BE \tag{5}$$

$$\frac{dF}{dt} = +2k_2BD + k_1BE - k_2BF \tag{6}$$

$$\frac{dG}{dt} = +k_2BF \tag{7}$$

By manipulation of these equations, it is possible to solve for the concentration of each component as a function of t. The number of sulphone groups present is constant, so:

$$A + C + D + E + F + G = A_0 \tag{8}$$

and

$$\frac{dA}{dt} + \frac{dC}{dt} + \frac{dD}{dt} + \frac{dE}{dt} + \frac{dF}{dt} + \frac{dG}{dt} = 0 \tag{9}$$

Similarly, the number of epoxide groups plus the number of —$CH_2CHOHCH_2$— groups is constant, so:

$$B + C + 2D + 2E + 3F + 4G = B_0 = 4fA_0 \tag{10}$$

and

$$\frac{dB}{dt} + \frac{dC}{dt} + 2\frac{dD}{dt} + 2\frac{dE}{dt} + 3\frac{dF}{dt} + 4\frac{dG}{dt} = 0 \tag{11}$$

Let x represent the concentration of primary amine groups present. Then:

$$x = 2A + C + E \tag{12}$$

and by using Eqs. 1, 3, and 5:

$$\frac{dx}{dt} = 2\frac{dA}{dt} + \frac{dC}{dt} + \frac{dE}{dt} = -k_1Bx \tag{13}$$

Similarly, let y represent the concentration of secondary amine groups. Then:

$$y = C + 2D + F \tag{14}$$

and by using Eqs. 3, 4, and 6:

$$\frac{dy}{dt} = \frac{dC}{dt} + 2\frac{dD}{dt} + \frac{dF}{dt} = +k_1Bx - k_2By \tag{15}$$

From Eq. 12:

$$E = x - 2A - C \tag{16}$$

From Eq. 14:

$$F = y - C - 2D \tag{17}$$

Substituting for E and F in Eq. 8 gives:

$$G = A_0 + A + C + D - x - y \tag{18}$$

Substituting for E, F, and G in Eq. 10 leads to:

$$B = 4(f-1)A_0 + 2x + y \tag{19}$$

and

$$\frac{dB}{dt} = 2\frac{dx}{dt} + \frac{dy}{dt} = -k_1Bx - k_2By \tag{20}$$

Substituting for y from Eq. 19 gives:

$$\frac{dB}{dt} = (2k_2 - k_1)Bx + k_2B\{4(f-1)A_0 - B\} \tag{21}$$

The degree of polymerization α is defined in terms of the number of unreacted epoxide molecules according to:

$$\alpha = 1 - \frac{B}{B_0} \tag{22}$$

and therefore:

$$B = B_0(1-\alpha) = 4fA_0(1-\alpha) \tag{23}$$

Substituting this equation into Eqs. 21 and 13 produces the following two equations in α and x, which may be solved for these two variables as a function of time:

$$\frac{d\alpha}{dt} = (k_1 - 2k_2)(1-\alpha)x + 4A_0k_2(1-\alpha)(1-f\alpha) \tag{24}$$

$$\frac{dx}{dt} = -4fA_0k_1(1-\alpha)x \tag{25}$$

To simplify the solution of these equations, we consider two simple cases.

SIMPLIFIED CASE NO. 1

We assume that all the N-H bonds have the same reactivity with respect to an epoxide group, that is to say:

$$k_2 = \tfrac{1}{2}k_1 \tag{26}$$

Then Eq. 24 simplifies to:

$$\frac{d\alpha}{dt} = 2A_0k_1(1-\alpha)(1-f\alpha) \tag{27}$$

The solution of this equation (with the initial condition $\alpha = 0$ when $t = 0$) is as follows:

$$\alpha = \frac{1 - \exp(-pt)}{f - \exp(-pt)} \tag{28}$$

where

$$p = 2A_0 k_1 (f - 1) \tag{29}$$

The solution for B in terms of α (and hence t) is given by Eq. 23.

Dividing Eq. 1 by Eq. 27 and substituting for B from Eq. 23 gives:

$$\frac{dA}{d\alpha} = \frac{-4fA}{1 - f\alpha} \tag{30}$$

which may be solved to give A as a function of α, subject to the initial condition $A = A_0$ when $\alpha = 0$:

$$A = A_0(1 - f\alpha)^4 \tag{31}$$

Similarly, dividing Eq. 3 by Eq. 27 and substituting for B from Eq. 23 gives:

$$\frac{dC}{d\alpha} = \frac{f(4A - 3C)}{1 - f\alpha} \tag{32}$$

After substituting for A from Eq. 31, this may be rearranged to give:

$$\frac{d}{d\alpha}\left\{(1 - f\alpha)^{-3} C\right\} = 4fA_0 \tag{33}$$

The solution, after applying the initial condition $C = 0$ when $\alpha = 0$, is:

$$C = 4fA_0\alpha(1 - f\alpha)^3 \tag{34}$$

This completes the solution for the most important components. The others could be obtained by a similar procedure if desired. To summarize:

$$\alpha = \frac{1 - \exp(-pt)}{f - \exp(-pt)} \qquad \text{where } p = 2A_0 k_1 (f - 1)$$

$$A = A_0(1 - f\alpha)^4$$

$$B = 4fA_0(1 - \alpha)$$

$$C = 4fA_0\alpha(1 - f\alpha)^3$$

SIMPLIFIED CASE NO. 2

This corresponds to the other extreme, that is to say, that the N-H bonds of the secondary amine groups do not react, or:

$$k_2 = 0 \tag{35}$$

Then Eq. 24 reduces to:

$$\frac{d\alpha}{dt} = k_1(1-\alpha)x \tag{36}$$

Dividing Eq. 25 by Eq. 36:

$$\frac{dx}{d\alpha} = -4fA_0 \tag{37}$$

When $t = 0$, $\alpha = 0$ and $x = 2A_0$, so the solution is:

$$x = 2A_0(1-2f\alpha) \tag{38}$$

Substituting in Eq. 36 gives:

$$\frac{d\alpha}{dt} = 2A_0k_1(1-\alpha)(1-2f\alpha) \tag{39}$$

The solution, applying the initial condition $\alpha = 0$ when $t = 0$, is:

$$\alpha = \frac{1-\exp(-qt)}{2f-\exp(-qt)} \tag{40}$$

where

$$q = 2A_0k_1(2f-1) \tag{41}$$

As in the previous case, B is given by Eq. 23.

Dividing Eq. 1 by Eq. 39 and substituting for B from Eq. 23 gives:

$$\frac{dA}{d\alpha} = \frac{-4fA}{1-2f\alpha} \tag{42}$$

which may be solved to give A as a function of α:

$$A = A_0(1-2f\alpha)^2 \tag{43}$$

Dividing Eq. 3 by Eq. 39 and substituting for B from Eq. 23 gives:

$$\frac{dC}{d\alpha} = \frac{2f(2A-C)}{1-2f\alpha} \tag{44}$$

After substituting for A from Eq. 43, this may be rearranged to give:

$$\frac{d}{d\alpha}\left\{(1-2f\alpha)^{-1}C\right\} = 4fA_0 \tag{45}$$

The solution, after applying the initial condition $C = 0$ when $\alpha = 0$, is:

$$C = 4fA_0\alpha(1-2f\alpha) \tag{46}$$

To summarize:

$$\alpha = \frac{1-\exp(-qt)}{2f-\exp(-qt)} \qquad \text{where } q = 2A_0k_1(2f-1)$$

$$A = A_0(1-2f\alpha)^2$$

$$B = 4fA_0(1-\alpha)$$

$$C = 4fA_0\alpha(1-2f\alpha)$$

DISCUSSION

Figures A-2 to A-5 show the predicted variation of some of these quantities for the two simplified cases, taking a typical value of 1.6 for f. The quantities plotted are A/A_0, C/A_0, B/A, and C/A. The quantity B/A_0 is of little interest since, by the definition of α according to Eqs. 22 and 23, it shows the same behaviour in both cases: a linear decrease with α. With $f = 1.6$, there is an excess of epoxy with respect to amine (the subsequent epoxy-hydroxyl reaction is neglected). For this reason, the reaction "stops" at $\alpha = f^{-1} = 0.625$ in Case 1 and $\alpha = (2f)^{-1} = 0.3125$ in Case 2. In both cases, the reaction product C reaches its maximum concentration at $\alpha = (4f)^{-1} = 0.156$. The graphs show that in the early stages of the reaction (i.e. for $\alpha < 0.1$) only the reaction between primary amine and epoxy is really significant and there is little difference between the two cases. We take Case 1 as the more likely possibility. In addition, within the range $0 < \alpha < 0.1$, the variation of the ratios B/A and C/A with α may be considered linear with a good degree of approximation. With these results in mind, we now consider the more complicated case where there is present a second epoxy resin with (possibly) different reactivity.

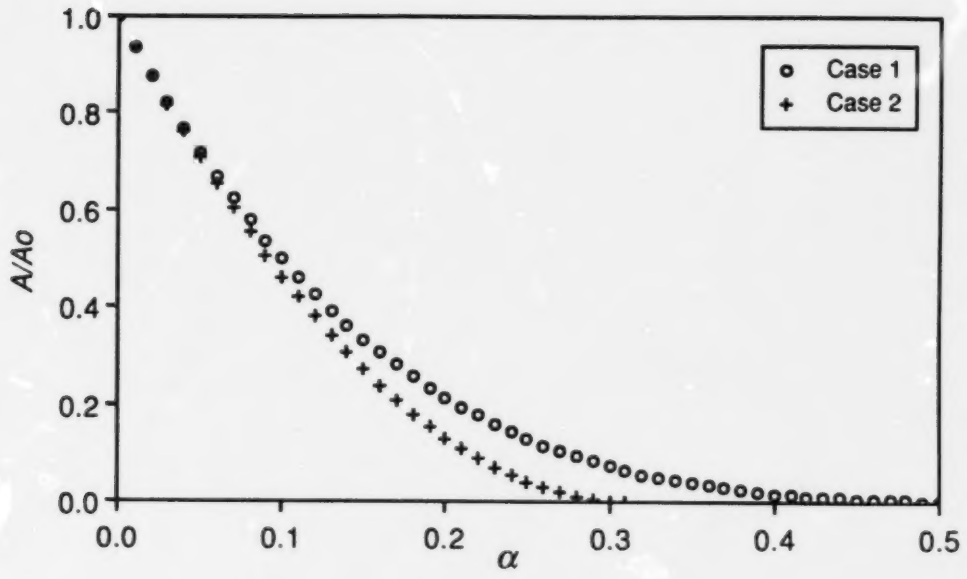

Figure A-2. Predicted variation of the DDS concentration as a function of α for the two simplified cases involving a single epoxy.

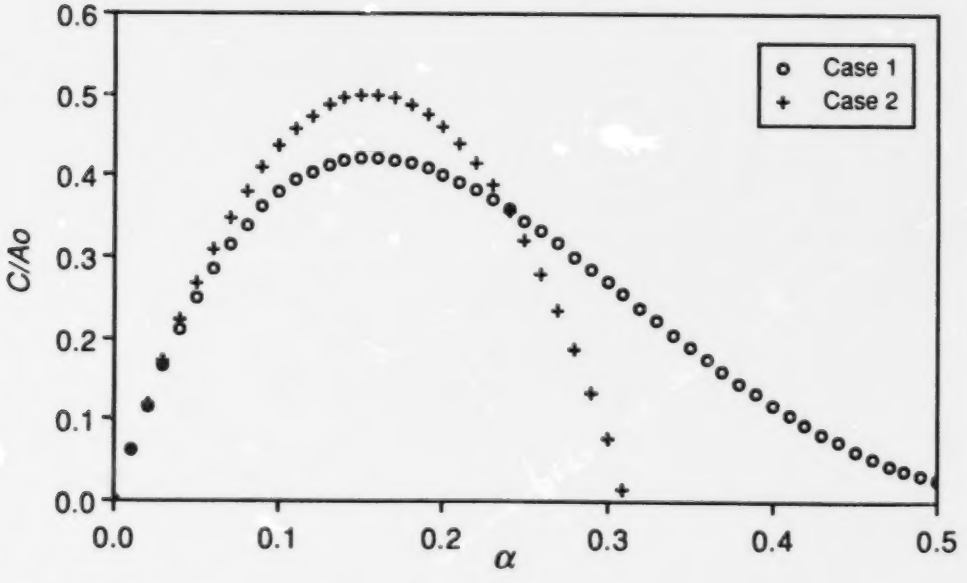

Figure A-3. Predicted variation of the initial reaction product concentration as a function of α for the two simplified cases involving a single epoxy.

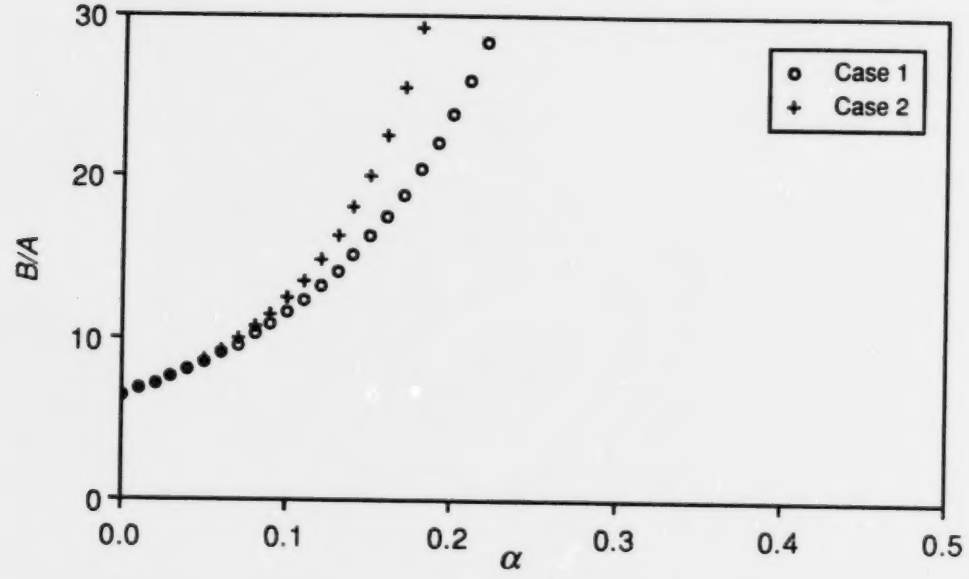

Figure A-4. Predicted variation of the epoxy/DDS ratio as a function of α for the two simplified cases involving a single epoxy.

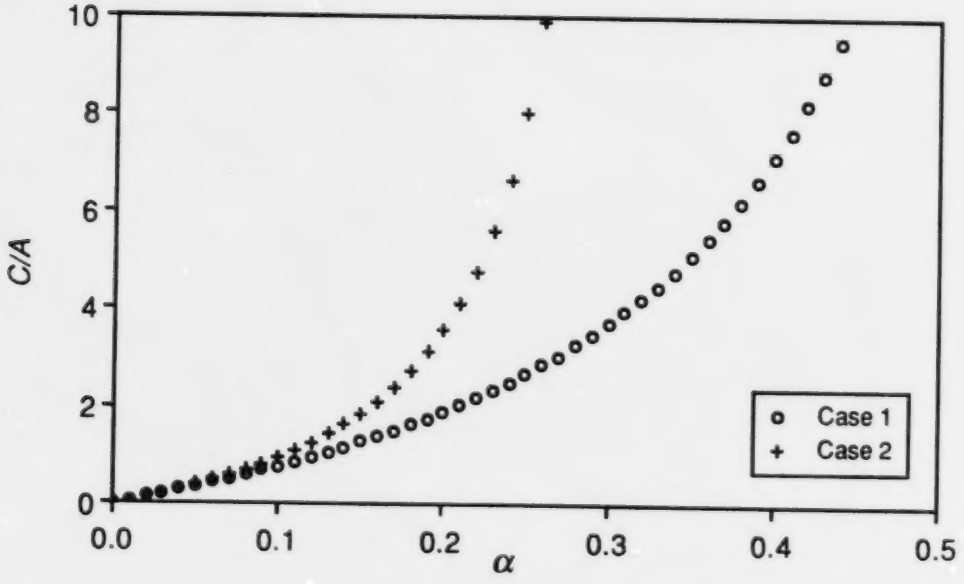

Figure A-5. Predicted variation of the reaction product/DDS ratio as a function of α for the two simplified cases involving a single epoxy.

EXTENSION TO TWO EPOXIES:

In keeping with the previous case, we represent the second epoxy by **B'**, its concentration at time t by B', and its initial concentration by B_0'. The epoxide-to-amine ratio (corresponding to f for the first epoxy) is defined by $g = B_0'/4A_0$, so the overall epoxide-to-amine ratio is $f + g$. We also define new rate constants k_1' and k_2' for the reactions of the second epoxy with primary and secondary amine groups respectively. The initial reaction product between **B'** and **A** is designated **C'**, with concentration C'. However, no distinction is made for subsequent reaction products **D**, **E**, **F**, and **G**, since these are not detected chromatographically. The general reaction scheme now becomes:

$$\mathbf{A} + \mathbf{B} \xrightarrow{2k_1} \mathbf{C}$$

$$\mathbf{A} + \mathbf{B}' \xrightarrow{2k_1'} \mathbf{C}'$$

$$\mathbf{B} + \mathbf{C} \xrightarrow{k_1} \mathbf{D}$$

$$\mathbf{B} + \mathbf{C} \xrightarrow{k_2} \mathbf{E}$$

$$\mathbf{B} + \mathbf{C}' \xrightarrow{k_1} \mathbf{D}$$

$$\mathbf{B} + \mathbf{C}' \xrightarrow{k_2} \mathbf{E}$$

$$\mathbf{B}' + \mathbf{C} \xrightarrow{k_1'} \mathbf{D}$$

$$\mathbf{B}' + \mathbf{C} \xrightarrow{k_2'} \mathbf{E}$$

$$\mathbf{B}' + \mathbf{C}' \xrightarrow{k_1'} \mathbf{D}$$

$$\mathbf{B}' + \mathbf{C}' \xrightarrow{k_2'} \mathbf{E}$$

$$\mathbf{B} + \mathbf{D} \xrightarrow{2k_2} \mathbf{F}$$

$$\mathbf{B}' + \mathbf{D} \xrightarrow{2k_2'} \mathbf{F}$$

$$\mathbf{B} + \mathbf{E} \xrightarrow{k_1} \mathbf{F}$$

$$\mathbf{B'} + \mathbf{E} \xrightarrow{k'_1} \mathbf{F}$$

$$\mathbf{B} + \mathbf{F} \xrightarrow{k_2} \mathbf{G}$$

$$\mathbf{B'} + \mathbf{F} \xrightarrow{k'_2} \mathbf{G}$$

and the kinetic equations are:

$$\frac{dA}{dt} = -2k_1AB - 2k'_1AB'$$

$$\frac{dB}{dt} = -2k_1AB - (k_1 + k_2)BC - (k_1 + k_2)BC' - 2k_2BD - k_1BE - k_2BF$$

$$\frac{dB'}{dt} = -2k'_1AB' - (k'_1 + k'_2)B'C - (k'_1 + k'_2)B'C' - 2k'_2B'D - k'_1B'E - k'_2B'F$$

$$\frac{dC}{dt} = +2k_1AB - (k_1 + k_2)BC - (k'_1 + k'_2)B'C$$

$$\frac{dC'}{dt} = +2k'_1AB' - (k_1 + k_2)BC' - (k'_1 + k'_2)B'C'$$

$$\frac{dD}{dt} = +k_1BC + k_1BC' + k'_1B'C + k'_1B'C' - 2k_2BD - 2k'_2B'D$$

$$\frac{dE}{dt} = +k_2BC + k_2BC' + k'_2B'C + k'_2B'C' - k_1BE - k'_1B'E$$

$$\frac{dF}{dt} = +2k_2BD + 2k'_2B'D + k_1BE + k'_1B'E - k_2BF - k'_2B'F$$

$$\frac{dG}{dt} = +k_2BF + k'_2B'F$$

As in the single-epoxy case, certain simplifications are necessary. We consider only the case where both primary and secondary N-H groups have the same reactivity with respect to an epoxide group. We also define by r the ratio of the reactivities of the two epoxies. Thus we let:

$$k_1 = k$$

$$k_1' = r k_1 = r k$$

$$k_2 = \tfrac{1}{2} k_1 = \tfrac{1}{2} k$$

$$k_2' = \tfrac{1}{2} k_1' = \tfrac{1}{2} r k$$

The kinetic equations then reduce to:

$$\frac{dA}{dt} = -2k\,A(B + rB') \tag{47}$$

$$\frac{dB}{dt} = -k\,B\left(2A + \tfrac{3}{2}C + \tfrac{3}{2}C' + D + E + \tfrac{1}{2}F\right) \tag{48}$$

$$\frac{dB'}{dt} = -r\,k\,B'\left(2A + \tfrac{3}{2}C + \tfrac{3}{2}C' + D + E + \tfrac{1}{2}F\right) \tag{49}$$

$$\frac{dC}{dt} = k\left[2AB - \tfrac{3}{2}C(B + rB')\right] \tag{50}$$

$$\frac{dC'}{dt} = k\left[2rAB' - \tfrac{3}{2}C'(B + rB')\right] \tag{51}$$

$$\frac{dD}{dt} = k\,(B + rB')(C + C' - D) \tag{52}$$

$$\frac{dE}{dt} = k\,(B + rB')\left(\tfrac{1}{2}C + \tfrac{1}{2}C' - E\right) \tag{53}$$

$$\frac{dF}{dt} = k\,(B + rB')\left(D + E - \tfrac{1}{2}F\right) \tag{54}$$

$$\frac{dG}{dt} = \tfrac{1}{2}k\,F(B + rB') \tag{55}$$

To solve these equations, we proceed in a manner similar to the single-epoxy case. Since the number of sulphone groups present is constant:

$$A + C + C' + D + E + F + G = A_0 \tag{56}$$

Similarly, the number of epoxide groups plus the number of —$CH_2CHOHCH_2$— groups is constant, so:

$$B + B' + C + C' + 2D + 2E + 3F + 4G = B_0 + B_0' = 4(f + g)A_0 \tag{57}$$

Let x represent the concentration of primary amine groups present. Then:

$$x = 2A + C + C' + E \tag{58}$$

and by using Eqs. 47, 50, 51, and 53:

$$\frac{dx}{dt} = -k\,x(B + rB') \tag{59}$$

Similarly, let y represent the concentration of secondary amine groups. Then:

$$y = C + C' + 2D + F \tag{60}$$

and by using Eqs. 50, 51, 52, and 54:

$$\frac{dy}{dt} = k(B + rB')(x - \tfrac{1}{2}y) \tag{61}$$

From Eq. 58: $$E = x - 2A - C - C' \tag{62}$$

From Eq. 60: $$F = y - C - C' - 2D \tag{63}$$

Substituting for E and F in Eq. 56 gives:

$$G = A_0 + A + C + C' + D - x - y \tag{64}$$

Substituting for E, F, and G in Eq. 57 leads to:

$$B + B' = B_0 + B_0' - 4A_0 + 2x + y \tag{65}$$

and hence $$\frac{d}{dt}(B + B') = 2\frac{dx}{dt} + \frac{dy}{dt} = -k(B + rB')(x + \tfrac{1}{2}y) \tag{66}$$

Substituting for y from Eq. 65 gives:

$$\frac{d}{dt}(B + B') = \tfrac{1}{2}k(B + rB')(B_0 + B_0' - 4A_0 - B - B') \tag{67}$$

From a comparison of Eqs. 48 and 49, it is seen that:

$$\frac{1}{B}\frac{dB}{dt} = \frac{1}{rB'}\frac{dB'}{dt} \tag{68}$$

which is easily solved to give:

$$\frac{B'}{B_0'} = \left(\frac{B}{B_0}\right)^r \tag{69}$$

On substituting in Eq. 67, we obtain:

$$\frac{dB}{dt} = \frac{1}{2}k\,B\left\{B_0 + B_0' - 4A_0 - B - B_0' B_0^{-r} B^r\right\} \tag{70}$$

An exact solution for B as a function of t is not possible. However, since we are interested only in small values of α, a series expansion can be used. The result is:

$$\frac{B}{B_0} = 1 - 2(kA_0 t) + 2\left\{1 + \frac{B_0 + rB_0'}{4A_0}\right\}(kA_0 t)^2 + \ldots \tag{71}$$

By applying Eq. 69, we also obtain:

$$\frac{B'}{B_0'} = 1 - 2r(kA_0 t) + 2r\left\{r + \frac{B_0 + rB_0'}{4A_0}\right\}(kA_0 t)^2 + \ldots \tag{72}$$

As before, the degree of polymerization α is defined in terms of the total number of unreacted epoxide molecules according to:

$$\alpha = 1 - \frac{B + B'}{B_0 + B_0'} \tag{73}$$

We can thus calculate α as a function of t using Eqs. 71 and 72. Making the substitutions $B_0 = 4fA_0$ and $B_0' = 4gA_0$, we obtain:

$$\alpha = 2\left\{\frac{f + rg}{f + g}\right\}(kA_0 t) - 2\left\{\frac{(f + rg)^2 + f + r^2 g}{f + g}\right\}(kA_0 t)^2 + \ldots \tag{74}$$

In the case of A, we can obtain an exact solution in terms of α. Combining Eqs. 67 and 73 gives:

$$\frac{d\alpha}{dt} = \frac{1}{2}k\,(B + rB')\left(\frac{1}{f + g} - \alpha\right) \tag{75}$$

and dividing this into Eq. 47 gives:

$$\frac{dA}{d\alpha} = \frac{-4A}{\frac{1}{f + g} - \alpha} \tag{76}$$

This is easily solved to give:

$$\frac{A}{A_0} = [1 - (f + g)\alpha]^4 \tag{77}$$

or in terms of t:

$$\frac{A}{A_0} = 1 - 8\{f + rg\}(kA_0t) + 8\left\{f + r^2g + 4(f + rg)^2\right\}(kA_0t)^2 + \ldots \quad (78)$$

With these results we can use Eqs. 50 and 51 to solve for C and C' as series in t. The results are:

$$\frac{C}{A_0} = 8f(kA_0t) - 8f\{1 + 7(f + rg)\}(kA_0t)^2 + \ldots \quad (79)$$

$$\frac{C'}{A_0} = 8rg(kA_0t) - 8rg\{r + 7(f + rg)\}(kA_0t)^2 + \ldots \quad (80)$$

Finally, by making use of Eq. 74, it is possible to express the concentration of each component in terms of α. The results may then be summarized as follows:

$$A = A_0[1 - (f + g)\alpha]^4 \quad (81)$$

$$B = 4fA_0\left[1 - \frac{f + g}{f + rg}\alpha + \frac{rg(1 - r)(f + g)^2}{2(f + rg)^3}\alpha^2 + \ldots\right] \quad (82)$$

$$B' = 4gA_0\left[1 - \frac{r(f + g)}{f + rg}\alpha + \frac{rf(r - 1)(f + g)^2}{2(f + rg)^3}\alpha^2 + \ldots\right] \quad (83)$$

$$C = 4fA_0\left[\frac{f + g}{f + rg}\alpha + \frac{(f + g)^2}{2(f + rg)^3}\left\{rg(r - 1) - 6(f + rg)^2\right\}\alpha^2 + \ldots\right] \quad (84)$$

$$C' = 4rgA_0\left[\frac{f + g}{f + rg}\alpha + \frac{(f + g)^2}{2(f + rg)^3}\left\{f(1 - r) - 6(f + rg)^2\right\}\alpha^2 + \ldots\right] \quad (85)$$